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Hydrocarbon Pollutant Systems Study

Vol. 1 stationary sources, effects, and control

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Research Triangle Park, North Carolina 27711

on

HYDROCARBON POLLUTANT SYSTEMS STUDY

Volume I - Stationary Sources, Effects, and Control

October 20, 1972

MSA RESEARCH CORPORATION
Evans City, Pennsylvania

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16. Abstracts The study was conducted to develop a problem-solving R & D program for the control of hydrocarbon air pollutants from major stationary sources. A systems study approach was used in which the desired outputs were incorporated into a preliminary systems model. The major input categories are listed as follows, as applied to the systems model: (1) Major sources and emissions - the technical literature and reports of related government contracts provided emission factors that relate amounts and types of emissions to the quantities of materials processed by the major source categories. These factors were applied to published statistics and estimates of quantities processed to quantify source category emissions; (2) Ranking of adverse effects. A review of the literature revealed that the most frequently documented instances of vegetation and material damage and of human discomfort are due to photochemical smog. Therefore it is the principal parameter used to rank pollutants and sources; (3) Control of hydrocarbon emissions - a general review of the control art was made to identify existing control techniques for which economic evaluations should be made. Deficiencies in these technologies were studied; (4) R & D program - specific data deficiencies were identified. Recommendations were developed using priorities based on source ranking, technological deficiencies and control costs.

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SUMMARY

This summary presents the results and conclusions of the Hydrocarbon Pollutant Systems Study. An overview of the total study is followed by summaries of the major report sections.

Hydrocarbon air pollutants are emitted by the major stationary sources in significantly greater quantities than previously estimated. The total quantity of hydrocarbons emitted to the atmosphere is estimated in this study to be in excess of 25 million tons per year, but this estimate provides only a part of the hydrocarbon pollution picture. At concentrations measured in ambient air, the non-photochemically reactive hydrocarbon pollutants demonstrate no apparent serious health threat. The major harmful effects of hydrocarbon emissions result from their contribution to photochemical smog, which is known to have adverse effects on humans, vegetation and materials.

Photochemically reactive hydrocarbon emissions are estimated to constitute about 20 percent of total annual hydrocarbon emissions. These reactive hydrocarbons are derived primarily from organic solvent evaporation, gasoline storage and marketing, solid waste combustion, agricultural burning of crop and field residues, and to a lesser extent, petroleum production and refining.

A state-of-the-art review of control technology shows that hydrocarbon emissions could be significantly reduced by proper and widespread application of available control techniques. More specifically, emissions from uncontrolled sources could be reduced at least 50 percent by application of available technology.

Certain available control techniques could and should be improved; an R&D program to develop these improvements and to fill other technology needs is recommended. Specific R&D programs to improve characterization and monitoring of emissions; documentation of adverse effects; and interdisciplinary studies of air, water and solid waste pollution are also recommended. For source categories that are not directly amenable to applied controls (eg., the open burning of solid and liquid wastes) or that can be modified to reduce the amount of control necessary (eg., solvent evaporation sources), alternative practices and process modifications are suggested.

Insufficient quantitative data were available for completion of a generalized systems model that would provide the socio-economic benefit/cost relationships for application of various control technologies to a given hydrocarbon pollutant source. Engineering cost studies do show, however, that economic payout can be achieved in some applications of control systems. Control techniques that do not offer payouts can generally be applied without severe economic penalties.

Ranking of Pollutants and Sources

An attempt was made to combine emissions data with data from a review of adverse effects to provide generalized source-effect rankings and geographical distribution. Identifiable adverse health effects of hydrocarbon pollutants were so limited, however, that relative health effects rankings could not be justified. Certain pollutants can be identified as potentially hazardous, particularly to predisposed segments of the population. Sensory irritation and aggravation of existing respiratory ailments can result from chronic exposure to low concentrations of formaldehyde and acrolein. Laboratory studies of the polycyclic aromatic hydrocarbons, particularly benzo-a-pyrene, have shown potential carcinogenic activity, and although not specific, epidemiological studies have revealed an urban factor that probably results from the emission of greater amounts of polycyclic aromatic hydrocarbons in urban areas.

Because of the lack of data on adverse effects of hydrocarbon pollutants specifically, the major factor utilized in ranking pollutants and sources was photochemical reactivity, or relative smog contribution. Specific compounds and some general chemical classifications have been demonstrated to be photochemically reactive in smog chamber studies and thus are principal contributors to smog. Application of reactivity parameters to the hydrocarbon sources and their total emissions resulted in the relative rankings shown in Table 1.

Investigation of the geographical distribution of the major sources shows that certain categories, particularly gasoline storage and marketing and solid waste combustion, are highly population density dependent and thus are a widespread urban problem. Other sources are more closely related to industrial processes; these sources may be generally widespread, as are industrial solvent evaporation sources, or they may be highly localized, as are petroleum refining and petrochemical operations.

Table 1 - "Best Estimate" Reactivity Ranking of Major Emission Sources

Source Category	Total Hydrocarbon Emissions 10^6 tons/yr	"High Reactivity" Emissions 10^6 tons/yr
Solvent Evaporation	7.1	1.9
Solid Waste Combustion (urban, domestic, commercial, and industrial)	4.5	1.4
Agricultural Waste Combustion	4.2	1.1
Petroleum Products Storage and Marketing	2.3	1.0
Petroleum Production and Refining	1.9	0.2
Chemical Process Industry	1.4	negligible
Other Industrial Processes	∿1	negligible
Fuel Combustion	0.4	negligible
Coal Refuse Burning	0.2	not estimated
Forest Wildfires	2.4-3.0	not estimated
Totals	25.4-26.0	5.6

The necessary conditions for formation of photochemical smog are highly dependent on local meteorological conditions and geographical features. Reviews of meteorological variations and ambient air monitoring data show that the highly urbanized regions of California are most affected by smog problems. Other major urban areas are much less affected by severe smog conditions. However, almost all urban areas are affected, at least a few times a year, by excessive smog manifestations.

Vegetative damage from hydrocarbon air pollution results primarily from photochemical reaction and, to a lesser extent, from ethylene emissions. Ozone, peroxyacetyl nitrate, and ethylene have been estimated to account for nearly 80 percent of total crop damage from air pollution in California. Other areas of the country are much less affected, but oxidants and ethylene do contribute significantly to total U.S. crop damage.

Materials damage, although not widely investigated or reported, does result from exposure of paint, rubber and plastics to photochemical oxidants.

Major Sources and Their Emissions

Estimates of total hydrocarbon emissions were obtained by application of selected emission factors to the amounts of material processed by the major source categories. Fuel combustion, solid waste combustion, solvent evaporation, petroleum refining and marketing, chemical processing, and some miscellaneous industrial sources were analyzed in this fashion.

Emission data for many sources are limited to estimates of total hydrocarbons, with little or no identification of specific chemical compounds or groups making up the total emission. Where possible, estimates of composition were derived from published data, so that emission and adverse effects data could be correlated.

The total emissions estimated for each of the major source categories were included in Table 1, given in the previous discussion of relative ranking by smog contribution.

Adverse Effects

General reviews of the literature on human health hazards, photochemical reactivity and vegetation damage were made to provide input for the ranking of pollutants and sources.

Reported data on human health effects of hydrocarbons are related primarily to industrial workroom exposure and thus only indirectly relate to chronic, ambient air exposures. Available data on chronic exposure to low concentrations of hydrocarbons do not, however, demonstrate a significant health hazard from hydrocarbon emissions. Low molecular weight oxygenated species, such as formaldehyde and acrolein, have been noted to produce sensory and upper respiratory irritation at low concentrations. Laboratory studies, supported circumstantially by epidemiological studies, show a potential human health hazard from exposure to polycyclic aromatic hydrocarbons; some of which have been shown to be carcinogenic in skin application studies of experimental animals.

Experimental data (i.e., hydrocarbon consumption, oxidation rates, and eye irritation) from smog chamber studies were correlated to give a Composite Reactivity Index. Major organic compounds found or expected to be present in ambient air are ranked on a scale of relative reactivity of from 0 to 10. Olefins, substituted aromatics and certain oxygenated compounds constitute the most highly reactive groupings.

A reveiw of vegetative damage by hydrocarbons shows predominant contributions by ethylene and photochemical oxidants. Exposure-injury relationships are reviewed and typical injury patterns described. Economic cost data on vegetative damage were found to be limited to estimates for a few states and areas. Synergistic interactions and problems of distinguishing injury patterns make the estimates highly speculative.

Systems Model

A generalized benefit/cost model is developed and illustrated. The lack of quantitative input data prevented completion of the functional benefit/cost relationship except in hypothetical terms. The model does provide the basis for accurate cost/benefit estimates of pollution in future investigations.

The model examines damage caused by emissions in five basic categories: human, material, animal, vegetable, and indirect. Damage functions are formulated and distributed to allow the total net function to be computed for a given stationary source. Application of respective control costs then allows development of benefit/cost matrices.

Although incomplete, the model does point out the need for future studies to overcome data deficiencies.

Control Technology

The state-of-the-art of current control technology is reviewed. Deficiencies in existing techniques are identified, and specific studies of wet scrubbing design and correlation are presented. A novel and highly useful procedure for correlation of particulate removal performance of wet scrubbing devices is developed.

General case cost estimates are presented for gasoline storage tank control, waste gas incineration, solvent adsorption, and wet scrubbing of particulate and soluble organics emissions. The effects of process ranges and heat recovery alternatives on capital and operating costs are considered.

Floating roof controls for gasoline storage tanks and solvent adsorption with recovery demonstrate significant economic payouts. Waste gas incineration costs are shown to be highly dependent on waste heat recovery and effluent concentration. For effluent concentrations in the range from about 13 to 18 percent of lower explosive limit (LEL), the operating costs of catalytic and thermal incineration are approximately equal. Analysis of cost data trends indicates that catalytic incineration is more economical at concentrations below this range and less economical at higher concentrations. At concentrations equivalent to 25 percent LEL and capacities in excess of 10,000 SCFM, heat recovery from thermal incineration can provide economic payout in 10 years or less.

Process modifications and various control alternatives are considered in relation to their potential for emission reduction. Existing and developable systems for solid waste disposal are treated briefly. Generalized cost considerations show that selection of an optimum disposal system to replace open burning depends on several factors. Transportation costs, land availability, waste types, and collection procedures require individual studies for specific regions.

Growth projections indicate hydrocarbon emissions, if uncontrolled, will increase about 3 to 5 percent annually. Widespread application of existing control technology can result in significant emission reduction, based on reported experience in California. San Francisco Bay Area studies show that controls being used have reduced total emissions from stationary sources nearly 70 percent. Controls in effect in 1969 reduced potential organic emissions from stationary sources 52.5 percent. A complete ban on backyard waste burning in effect in 1970 will further increase control effectiveness in the Bay Area.

R&D Recommendations

The identification and ranking of sources and types of hydrocarbon emissions and their adverse effects delineated areas for which application of control would result in significant benefit. However, much further study is needed to allow quantitative determination of the cost/benefit relationships of specific strategies for control of hydrocarbon emissions. To aid in future planning, a $5 million, 5-year program is presented, emphasizing those research areas in which current information is deficient.

The following major areas are recommended for research and development:

> Emissions and Sources - Detailed characterization of specific sources and emissions is needed to provide a basis for quantitative assessment of adverse effects and for proper implementation of control planning. These studies require improved monitoring techniques and instrumentation to provide continuous and chemically specific emission analysis.
>
> Adverse Effects - Chronic toxicity and epidemiological studies are needed because our present knowledge of the health effects of hydrocarbon pollutants is incomplete. These programs should be complemented by smog chamber studies over a broad range of simulated atmospheres with exposure of human subjects to assess health manifestations. The rather tenuous relationship of ambient air hydrocarbon levels to photochemical oxidant concentrations should be clarified and

refined by correlative investigation of meteorological and air sampling data.

Control Technology - Studies are needed to correct deficiencies in current control technology. These include investigations of the performance, in terms of control effectiveness or efficiency of removal of afterburners (both thermal and catalytic) and wet scrubbers for particulate removal. Other recommended R&D programs include studies to expand the design base and range of application of carbon adsorption, to improve the combustion efficiency of waste gas afterburners, and to update the data base for estimation of storage losses.

The rapidly expanding and changing status of control application requires that a program be initiated to revise and update, on a continuing basis, a comprehensive engineering manual for use by both plant engineers and control agency personnel. Finally, studies are recommended to integrate the efforts of air pollution control implementation with other efforts toward improvement of the total environment. These studies would examine and recommend steps to correct or avoid problems of water pollution or solid waste disposal resulting from air pollution control.

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I. INTRODUCTION

A. PURPOSE AND SCOPE OF STUDY

This study of hydrocarbon air pollutants was conducted for the Office of Air Programs of the Environmental Protection Agency under Contract Number EHSD 71-12. The study was performed by MSA Research Corporation, Evans City, Pennsylvania with the assistance of four subcontractors: Industrial Health Foundation, University Science Center, and Patent Development Associates, all of Pittsburgh; and Singmaster and Breyer of New York, New York.

The study goal was the development of a problem-solving R&D program for the control of hydrocarbon air pollutants from major stationary sources. The primary goal required the accomplishment of four major objectives:

(1) Identification, characterization and ranking of all significant stationary sources of hydrocarbon emissions.

(2) Characterization of the effluent streams from the major sources of hydrocarbon emissions.

(3) Evaluation, both technical and economic, of existing and developable technology for control of hydrocarbon emissions.

(4) Development of R&D priorities and recommendations for a program that will ultimately lead to proven control hardware and technology.

For the purpose of this study, the term hydrocarbons included all organic compounds, such as alcohols, acids, aldehydes, esters and halides. Also included were such borderline inorganic compounds as perchloroethylene. Specifically excluded from the study were the mercaptans and other compounds whose predominant pollutant characteristic is odor.

As a result of preliminary consultation with the EPA Project Officer, the major work emphasis was placed on Objective (1), above; the identification and ranking of sources and emissions. The approximate distribution of effort, expressed as percent of total manhours, was as follows:

Objective (1) - 75%

Objective (2) - 6%

Objective (3) - 12%

Objective (4) - 7%

B. BACKGROUND

In earlier studies of hydrocarbon air pollutants, total emissions from major stationary sources were estimated to be of the same order of magnitude as those from mobile sources. The Nationwide Inventory of Air Pollutant Emissions, 1968 (U.S. Department of Health, Education and Welfare, 1970) estimated stationary source hydrocarbon emissions at 15.4 million tons per year and mobile source emissions at 16.6 million tons per year for 1968. This study was undertaken to delineate the quantities, types and adverse effects on human health and welfare of the major source hydrocarbon emissions in greater detail, and further, to review the control art and provide recommendations for future, control-oriented R&D programs.

To achieve the study objectives, the project team proposed the utilization of a systems study approach in which the desired outputs, as defined by the Scope of Work provided by EPA, were incorporated into a preliminary systems model. Identification of the input data necessary to complete the functional relationships of the model thus provided a starting point for the survey of available information. The major data input categories and their application to the systems model are discussed briefly in the following paragraphs.

1. Major Sources and Emissions

The technical literature and reports of related government contracts provided emission factors that relate amounts and types of emissions to the quantities of materials handled or processed by the major source categories.

These factors were applied to published statistics and estimates of quantities processed to quantify source category emissions.

For many of the major sources, published data included only estimates of total hydrocarbon emissions. Where no data were available on the individual species or chemical groups making up the total, data from laboratory studies, simulated source studies, and field tests of similar processes or operations were used to estimate emissions of specific chemical entities.

2. Ranking of Adverse Effects

Estimates of total hydrocarbon emissions are significant only if related to some adverse effect on human health and welfare. A review of the literature on human health effects of hydrocarbons at concentration levels observed or estimated to be attainable in the ambient atmosphere revealed few documented instances of adverse effects on human health. Vegetation and materials are damaged by exposure to a few specific hydrocarbon compounds, but more often by exposure to secondary pollutants resulting from photochemical reaction of hydrocarbons with other pollutants to form photochemical smog. Because photochemical smog contributes to human discomfort and is known to damage vegetation and materials, it is the principal parameter used in this study to rank pollutants and sources.

Quantitative data on the socio-economic costs of the adverse effects of hydrocarbon pollutants were insufficient to complete a functional systems model.

3. Control of Hydrocarbon Emissions

A general review of the control art was made to identify those existing control techniques for which economic evaluations should be made. A second purpose of the review was to identify deficiencies in the control technology. Deficiencies in the design bases and fundamental mechanisms of wet scrubbing devices led to a more detailed study of this technology.

Economic studies were made of the most generally applicable control techniques. Industrial case histories were utilized for the economic evaluation, and ranges of pertinent operating perameters were investigated for their effect on capital and operating costs.

4. R&D Program

The hypothetical systems model relationships were used to identify specific data deficiencies that need to be overcome in future studies. Consideration of priorities based on source rankings along with technological deficiencies and control costs permitted development of recommendations for basic and applied R&D, as well as alternative methods that could be used to reduce hydrocarbon emissions.

II. RANKING OF POLLUTANTS AND SOURCES

A. INTRODUCTION

Identification and quantification of the major hydrocarbon pollutants and their sources on a national scale serve to define the total magnitude of the problem. However, to place these data in perspective and to allow priorities to be assigned for future R&D and control application, relative rankings were developed in terms of the adverse effects of these emissions and their geographical distribution.

In Chapter III, we present detailed estimates of the total organic emissions from the major source categories and, give breakdowns of their geographical distribution. The total organic emissions from these sources are summarized in Table II-1, ranked in the order of total quantity of emissions. The total estimated emissions of about 25 million tons/year are significantly higher than earlier estimates of about 15 million tons/year from stationary sources (U.S. Department of Health, Education and Welfare, 1970).

In the following sections of this chapter, we discuss pollutants from specific sources and their adverse effects. Adverse effects considered were human health effects, photochemical smog contribution, vegetative damage and some minor effects on materials.

B. HEALTH EFFECTS

1. General

Human health effects are of paramount importance in any consideration of the adverse effects of air pollutants. This fact has been recognized and emphasized by Congress in its enactment of legislation authorizing the Environmental Protection Agency to promulgate standards of ambient air quality and to expedite the control of air pollutant emissions.

In the review of the human health effects presented in the Air Quality Criteria for Hydrocarbons (U.S. Department of Health, Education and Welfare, 1970), it was found that there is little documented evidence that hydrocarbon air pollutants alone have adverse effects on the

Table II-1 Total Estimated Hydrocarbon Emissions From Stationary Source Categories

Source Category	Total Hydrocarbon Emissions 10^6 tons/yr
Solvent Evaporation	7.1
Solid Waste Combustion (urban, domestic, commercial and industrial)	4.5
Agricultural Waste Combustion	4.2
Petroleum Products Storage and Marketing	2.3
Petroleum Production and Refining	1.9
Chemical Process Industry	1.4
Other Industrial Processes	∿1
Fuel Combustion	0.4
Coal Refuse Burning	0.2
Forest Wildfires	2.4-3.0
Totals	25.4-26.0

health of the general public. Our review of the literature essentially confirmed this finding.

Documented health effects are limited to eye and respiratory irritation from exposure to the low molecular weight aldehydes and the organic peroxide and peroxy nitrate derivatives from photochemical reaction. Additionally there is widespread concern over the potentially carcinogenic effects of human exposure to the airborne polycyclic aromatic hydrocarbons.

2. Aldehydes and Smog Products

From our review of the health effects of the major identified emissions and also of general organic chemical group classifications, the only reported health effects attributable to exposure to concentration levels approaching those found in ambient air samples are eye and upper respiratory irritation observed on expsoure to the low molecular weight aldehydes, particularly acrolein and formaldehyde. Presence in the atmosphere of these aldehydes is the result of both direct emission from sources such as combustion of fuels and wastes and the secondary or photochemical reactions of reactive hydrocarbon emissions. Other photochemical reaction products having similar irritant effects are the organic peroxides and peroxy nitrates generally lumped with ozone as atmospheric or "total" oxidants.

Smith (1962) and Fassett (1963) reported findings of sensory irritation on short term exposure to concentrations in the range of from 2 to 4 ppm for formaldehyde and as low as 0.25 ppm for acrolein. These concentrations are significantly higher than those reported in ambient air but could be readily achieved in localized areas near emission sources. For example, Feldstein et al (1963) reported estimated concentrations of from 1 to 3 ppm of formaldehyde one to two miles downwind of a large (2000 tons) open burn of land clearing debris.

Although some aldehyde emissions result from chemical manufacture and processing, by far the largest emissions of formaldehyde and other low molecular weight aldehydes result from incomplete oxidation in the combustion of fuels and wastes. For example, total estimated emissions of aldehydes from fuel combustion are over 90 x 10^3 tons/year. Inefficient combustion of solid wastes can result in aldehyde emissions which range from 10 to 30 percent of the total organic emissions (Duprey, 1968; Feldstein, 1963).

Both formaldehyde and acrolein have been identified as products from photochemical reaction (Altshuller, 1966). Other photochemical products identified in smog chamber studies are the various organic peroxides and peroxy nitrates. Peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate have been shown in smog chamber studies to be potenti eye irritants. The presence of PAN has been demonstrated in ambient air. However, according to Renzetti and Bryan (1961), it does not exist in sufficient concentration to account for the degree of eye irritation experienced. It has also been suggested (Smith, 1965) that exposure to PAN under conditions of exercise stress results in increased oxygen uptake.

The wide variety of both organic and inorganic compounds present in smog effectively prevent singling out specific compounds as contributors to specific noted adverse effects. The severe sensory irritation and aggravation of chronic respiratory ailments noted in smog areas is undoubtedly due to the combined and possibly synergistic effects of all species present during these periods of poor atmospheric ventilation.

3. Polycyclic Aromatic Hydrocarbons

Of considerable concern in relation to human health are the polycyclic aromatic hydrocarbons (PAH). Certain of these PAH compounds, which are generally associated with the particulate phase in various combustion and industrial process emissions, have been shown to produce carcinogenic activity on the skin of animals subjected to laboratory studies. Epidemiological studies have also indicated a correlation between the incidence of pulmonary cancer and exposure to atmospheres containing PAH. These studies are reviewed in detail in Chapter IV, but several conclusions and recommendations may be summarized here.

Even though most of the evidence relating to carcinogenicity of PAH compounds, particularly benzo-a-pyrene, has been obtained from skin application of extracts to experimental animals, the potential danger is such that known emission sources of PAH should be controlled. The potential sources of PAH emissions have been identified by Hangebrauck and coworkers (1964, 1965, 1967) as being primarily heat generation and waste combustion processes, as well as industrial processes which involve heat processing of coal or petroleum based products such as asphalt, coke, and coal tar.

Hangebrauck (1967), in summarizing experimental data from tests of various sizes and types of heat generation processes, showed that, in spite of the wide range of emission rates from any one process, a correlation exists between benzo-a-pyrene (BaP) emissions and the size or heat output of the furnace. The highest BaP emission rates occurred with the smaller units and decreased with increasing furnace output, presumably in relation to the efficiency of combustion. Although only limited data were available on oil and gas fired units, the results tend to emphasize that emission rates from coal fired units are higher than those from oil or gas fired units of similar size.

The influence of heat generation sources on the total PAH emissions is emphasized in studies involving sampling and analysis of atmospheric concentrations of PAH, such as reported by Sawicki (1960, 1962) and DeMaio and Corn (1966). In general, significantly higher concentrations of airborne PAH have been observed during winter months than during summer or non-heating months.

Studies of the formation of PAH compounds by combustion sources have shown that airborne PAH are almost entirely adsorbed on the particulate or soot phase, with negligible atmospheric existence of PAH vapors. Commins (1962, 1969), Mukai (1964) and Thomas (1968) have shown from laboratory studies that, at most, only trace amounts of true vapor phase PAH are emitted from combustion sources and then only in samples taken from very close to the combustion source. Thus, removal or control of particulate emissions should be effective in controlling atmospheric PAH emissions.

This latter conclusion is partially supported by reported analyses of PAH in emissions from industrial process and heat generation sources. Hangebrauck (1967) reported analyses of emissions before and after wet scrubber control of hot-road-mix asphalt processing. Total benzene-soluble organic emissions were reduced by about 50 percent by the combination dry cyclone and wet spray scrubber. BaP emissions were reduced from 1,350 $\mu g/m^3$ to <100 $\mu g/m^3$.

Hangebrauck (1967), Cuffe et al (1965), and Diehl et al (1967) reported data on PAH emissions from large coal-burning boilers. Cuffe and Diehl collected samples only after fly-ash collection and thus do not show the effect of particulate removal. Hangebrauck reported data from tests on two furnaces in which samples were taken both before and after fly ash collection by electrostatic precipitation. Three of these tests on a vertically-fired furnace showed negligible reduction of total benzene-soluble organics and BaP (one test showed higher emissions after the collector). The one test of a front-wall-fired furnace showed a 73 percent reduction of BaP emission rate by fly-ash collection.

Only limited conclusions may be drawn from these scant data, but it appears that the various particulate removal devices are not equally effective in removing PAH from source emissions.

Hangebrauck (1967) estimated annual BaP emissions from fuel combustion, waste combustion and selected stationary industrial sources, using emission factors derived from source testing data. In his estimate, residential and commercial usage of coal accounted for 410 tons (nearly 90 percent) of the total stationary source emissions of 461 tons. However, the base year used for his fuel usage distribution was not specified. U.S. Bureau of Mines (1968) statistics on consumer usage of coal show a marked decrease in retail deliveries to residential and commercial coal users in recent years (Table II-2). In 1968, coal usage accounted for only 4.2 percent of all fuel energy consumed by residential and commercial consumers.

From 1968 statistics (U.S. Bureau of Mines, 1968) for the distribution of fuel consumption by consumer class, we recalculated the BaP emissions from fuel combustion, using Hangebrauck's emission factors and percentage distribution of hand-fired and stoker fired residential coal furnaces. As discussed later in Chapter III, BaP emissions from the residential and commercial coal usage category are thus estimated at 203 tons/year. The decreasing trend in usage of coal for residential and commercial heating illustrated by U.S. Bureau of Mines data for recent years (Figure II-1) will gradually reduce the BaP emissions from this source category. However, efforts should be made to accelerate this trend away from coal usage in residential furnaces since this source segment could not sustain the economic impact of applied controls.

C. PHOTOCHEMICAL REACTIVITY

1. General

Studies of photochemical smog formation have shown that although hydrocarbons are essential smog precursors,

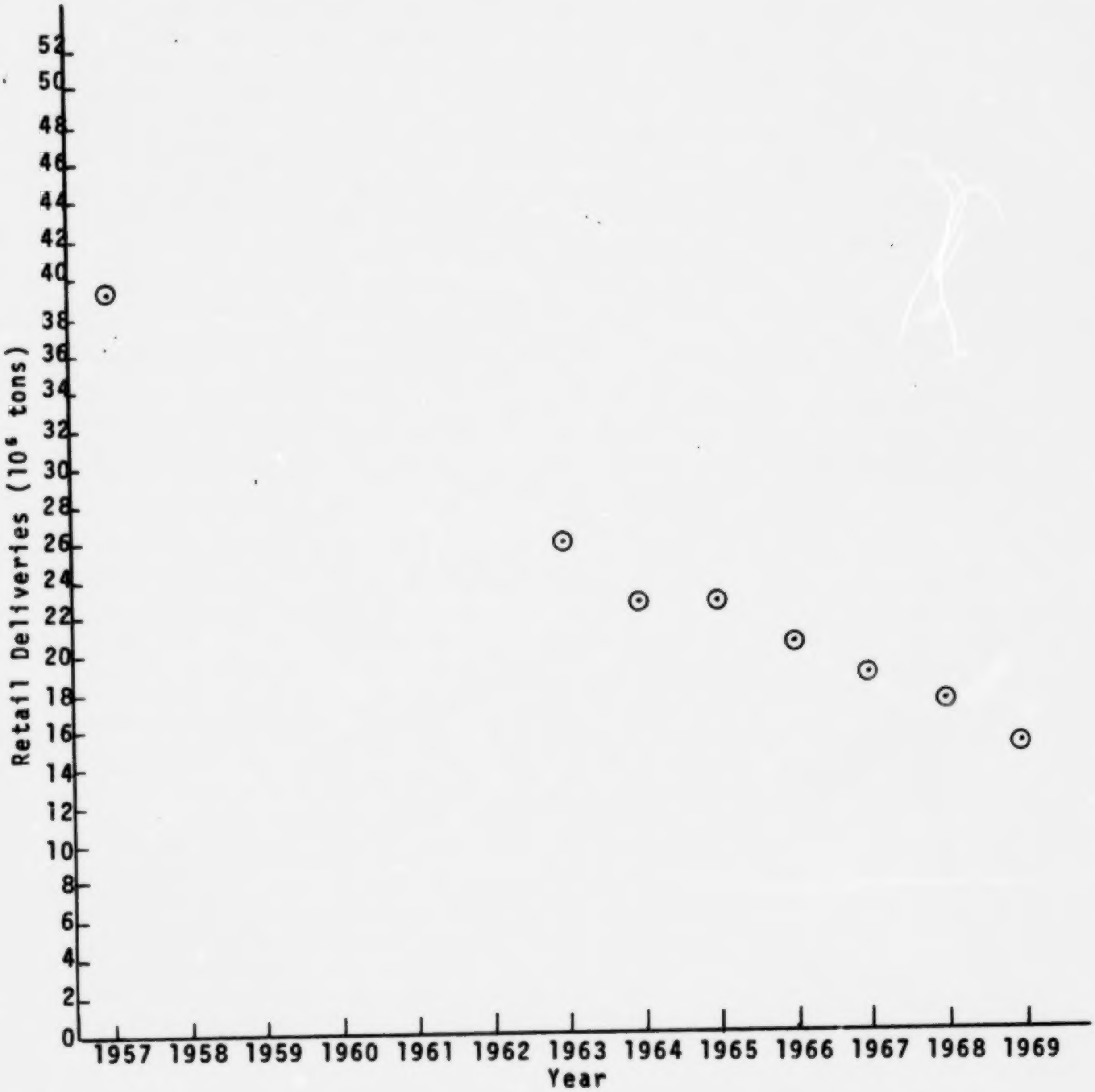

Figure II-1 - Annual Retail Deliveries of Bituminous Coal for Recent Years (from U.S. Bureau of Mines, 1969)

not all hydrocarbons undergo photochemical reaction to produce the physical manifestations of smog. As in any chemical reaction, differences in chemical structure and reactivity affect the reaction rates and resulting reaction products. Additionally, atmospheric reactions are complicated by synergistic interaction of air contaminants other than the usually considered smog precursors, hydrocarbons and nitrogen oxides (NO_x). Bufalini (1971) and Wilson and Levy (1970) have reviewed some of these synergistic interactions, particularly with respect to SO_2 oxidation and interaction.

As detailed in Chapter IV, the literature data on studies of the photochemical reactivity of the more prevalent organic air pollutants were correlated and compiled to give a composite reactivity index ranking. Such factors as nitric oxide oxidation rates, oxidant formation and eye irritation were considered in developing this reactivity index. These and additional studies have been further reviewed to develop more explicit ranking of the various pollutants and sources.

Some of the more recent studies of photochemical oxidation of hydrocarbons emphasize the highly arbitrary and uncertain nature of attempts to obtain definitive rankings of reactivity. Of particular interest are the studies by Altshuller et al (1969) and Bufalini et al (1971) on the oxidation of n-butane. Previous reviews and experimental studies were generally concentrated on reaction systems involving olefins and aromatics, since brief screening experiments had shown the saturated hydrocarbons to have very low reactivities. The work of Altshuller et al (1969) shows that under conditions of high enough ratios of hydrocarbon to NO_x significant photochemical reaction can take place. Bufalini et al (1971) have extended this work and shown that although the amount of saturated hydrocarbon reacted is low, significant oxidation of nitric oxide occurs. Reaction products common to other, more reactive systems are observed, such as ozone, peroxyacetyl nitrate, and aldehydes. Quoting from Altshuller (1971), "therefore it appears that almost every hydrocarbon except methane can produce some oxidant when photooxidized in the presence of high enough ratios of hydrocarbons to oxides of nitrogen."

2. Source Ranking

From studies made by the various air pollution control agencies in California, the California Air Resources

Board (1969) reported total organic emissions from the major source categories and also subdivided these total emissions into two groups as either "high" or "low" reactivity.* These ratings are based on the combined judgment of air pollution control personnel knowledgeable in smog control activities and thus should be given considerable weight. A mitigating factor on the use of these percentage high reactivity estimates is the probability that they reflect to some extent the distributions forced by legislative controls that are in effect in California, as compared with other regions of the United States.

For preliminary ranking purposes, the California data were reviewed and converted from the reported ton/day basis to a percentage basis for each of the major emission sources. The results are shown in Table II-3, as averages of data reported for the South Coast Air Basin (Los Angeles and neighboring counties) and the San Francisco Bay Area Air Basin.**

The percentage factors given in Table II-2 were used to rank the major source categories according to their relative "high" reactivity emissions, as shown in Table II-3. The two highest ranking source categories by this scheme are solvent evaporation and gasoline storage and marketing. Forest fires, which would also rank high, are not considered in this or further discussions because of their highly variable and uncertain nature and the lack of applicable control procedures.

a. Solvent Emissions - The 20 percent "high" reactivity classification for solvent evaporation emissions given by the California Air Resources Board (1969) was undoubtedly based on the control regulations in effect, since both the Los Angeles Rule 66 and the Bay Area Regulation 3 place an upper limit of 20 percent total reactive compounds in any solvent formulation being emitted. Thus, the use of 20 percent "high" reactivity may be too low to represent national solvent usage, which is generally not controlled by regulation.

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* "High reactivity" emissions are so classified by comparison of measured or estimated emission composition with the definitions of reactive hydrocarbons given by Los Angeles Rule 66 and Bay Area Regulation 3.

** Reported values for the San Diego Air Basin were not based on detailed emission inventory studies and thus were not used in the averaging of reactivity percentages.

Table II-2 - Reactivity Ranking of Stationary Source Organic Emissions (as percent of total emissions)*

Emission Source	% Reactivity High	% Reactivity Low
Petroleum		
Production	0	100
Refining	10	90
Marketing	45	55
Organic Solvent Users		
Surface Coating	20	80
Dry Cleaning	20	80
Degreasing	20	80
Other	20	80
Chemical Industries	0	100
Metallurgical Industries	0	100
Mineral Industries	0	100
Incineration		
Open burning, dumps	11	89
Open burning, backyard	11	89
Incinerators	11	89
Fuel Combustion		
Steam Power Plants	0	100
Other Industrial	0	100
Domestic and Commercial	0	100
Agriculture		
Debris Burning	11	89
Orchard Heaters	0	100
Agriculture Product Processing Plants (Bay Area values only)	0	100

*Based on California Air Resources Board (1969)

Table II-3 - Preliminary Reactivity Ranking of Major Emission Sources

Source Category	Total Hydrocarbon Emissions 10^6 tons/yr	"High Reactivity" Emissions 10^5 tons/yr
Solvent Evaporation	7.1	14.2
Petroleum Products Storage and Marketing	2.3	10.4
Solid Waste Combustion (urban, domestic, commercial and industrial)	4.5	5.0
Agricultural Waste Combustion	4.2	4.6
Petroleum Refining	1.7	1.7
Petroleum Production	0.2	negligible
Fuel Combustion	0.4	negligible
Chemical Process Industry	1.4	negligible
Other Industrial Processes	∿1	negligible
Forest Wildfires	2.4-3.0	not estimated
Coal Refuse Burning	0.2	not estimated

In order to arrive at a better or more representative estimate of solvent emissions reactivity, relative photochemical reactivity factors were derived for the specific compounds making up the total solvent emissions category. These reactivity factors are discussed in detail in Chapter IV, (page IV-27) but briefly, the methodology consists of assigning a numerical index, on a scale from 0 to 10, to the individual solvent according to data on its relative reactivity and eye irritant production under simulated smog conditions (smog chamber). These individual reactivity assignments were arithmetically averaged to achieve a Composite Reactivity Index.

Characterization of solvent emissions according to photochemical reactivity through the use of individual solvent reactivity indices is hampered by the uncertainties associated with definition of the reactivity of the solvent category of "special naphtha". "Special naphtha" is an all-inclusive term which includes all of the various petroleum fractions that are used in solvent-type applications. These petroleum fractions are generally classified by boiling range, aromatic content, and solvency, and may vary from narrow-boiling range, essentially single component fractions to highly complex mixtures tailored for specific applications.

Kirk-Othmer (1969) reported a total of 12 billion pounds of industrial solvents used in 1966 and gave the following breakdown by chemical groups: aliphatic hydrocarbons, 45%; aromatic hydrocarbons, 17%; chlorinated hydrocarbons, 13%; alcohols and esters, 10%; ketones, 8%; all others, 7%. Lunche et al (1957) gave a breakdown of solvents used in surface coatings in Los Angeles, aliphatic hydrocarbons accounted for 56.7% and aromatic hydrocarbons for 22.6%. They also gave sales volumes for the 11 most used solvents; aliphatic hydrocarbons accounted for 37.7% of the total volume.

Aliphatic and aromatic solvents are often so-classified on the basis of solvency tests, such as the kauri-butanol test (ASTM D 1133-54T), rather than on chemical composition. Aliphatic hydrocarbons thus classified have kauri-butanol numbers in the range 25 to 55 (pure toluene = 100) and aromatics have kauri-butanol numbers of greater than 55. Thus aliphatic hydrocarbons may have aromatic contents as high as about 30 percent. High naphthenic or cyclic paraffin content can however make this distinction less meaningful, since certain naphthenes can increase solvency without increasing aromaticity.

Because of the health hazard (in workroom atmospheres) associated with benzene and the generally higher solvency of the substituted aromatics, the benzene content of aromatic solvents is generally kept quite low. Thus, photochemical reactivity of special naphtha solvents may be based primarily on substituted aromatic content.

Mellan (1957, 1970) gives boiling range and composition data (as percent paraffin, naphthene and aromatic) for a number of commercial aliphatic and aromatic solvent formulations.*

From a review of the data on solvent composition and relative usage, we estimated the total "special naphtha" category as being 27 percent highly reactive.

By combining the above figure for the reactive fraction of special naphtha with the total usage of other solvents having a Composite Reactivity Index of 6 or higher, we arrived at a total estimated emission of highly reactive solvents of 38.4×10^8 lb/year, or approximately 27 percent of total solvent emissions. Based on this figure as more representing national usage, the total reactive solvent emissions are increased from 14.2×10^5 ton/year to 19.2×10^5 ton/year.

Among the many factors complicating ranking of industrial solvents is the widespread practice of baking industrial coatings at sufficiently high temperatures to produce photochemically reactive emissions from otherwise unreactive or slightly reactive solvent formulations. This problem has been recognized by both Los Angeles and Bay Area Control Districts, in that bake oven emissions must be controlled regardless of the exempt or non-exempt status of the solvent formulation used in the coatings application.

High temperature drying is a common production-line operation in several industries. Major examples include aircraft, furniture, metal can, appliance, and automotive painting. All types of surface coatings may be dried at elevated temperatures, with hydrocarbon emissions ultimately dependent upon the specific coating formulation and the elevated temperature drying conditions. Emissions are maintained below the "25% lower explosive limit" standard set by fire insurance underwriters, by diluting with air. Exhaust gases from high-temperature drying ovens contain partially oxidized and polymerized molecules in addition to the paint solvent species. Often these reaction products are present in the form of an aerosol in the exhaust. Solvents which contain long chain or unsaturated groups may be cleaved, forming aldehydes, ketones, or acids during their exposure to these high temperatures and oxidizing conditions.

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* The composition and reactivity of a number of commercial solvents has been listed in Bay Area Information Bulletin 1-69 (1969). Based on aromatic and olefin content and the definitions of Regulation 3, the solvents are classified as reactive, questionable or unreactive. Of the 143 solvents listed, 77 are reactive, 36 are questionable and 30 are unreactive. The listed solvents are almost entirely petroleum based solvents used for surface coating and analogous solvent usage, most of which would fall under the category of "special naphtha".

Thus, the ranking of a particular solvent as unreactive applies only for usage where little or no heat is applied during any subsequent drying or curing steps

b. Gasoline Evaporation Emissions - The California rating of gasoline evaporative losses as being 45 percent "high" reactive is probably based on the typical 40 to 50 percent total aromatic plus olefin content of most motor gasolines.

Maynard and Sanders (1969) have reported the determination of the composition and reactivity of some typical premium grade gasolines. Their detailed analysis of a premium grade fuel shows specific identification of 233 hydrocarbons. Their range of calculated reactivity, based on the summation of component reactivities, is 1.32 to 2.10. In order to be consistent with other approximations in this study, the reported analysis of one premium grade gasoline has been combined with our reactivity factors and a Composite Reactivity Index value developed. On the basis of major identified components, accounting for about 80 mol% of the total composition, a Composite Reactivity Index value of 2.2 was obtained, which is in reasonable agreement with the range given by Maynard and Sanders.

Two distinct problem areas make it difficult to predict the reactivity of gasoline emissions.

1. Modern trends toward the elimination of lead alkyls have resulted in increased blending of aromatics to improve octane ratings. The aromatic

compounds used, toluene and xylenes, have greater photochemical reactivities than most of the branched-chain alkanes. Eccleston (1970) reported combined aromatic and olefin contents of some prototype unleaded fuels of over 55 mol% (44.9 mol% aromatic, 10.7 mol% olefin).

2. The highly volatile components in gasolines have, in general, lower reactivities, but are probably released during the first storage and handling processes. Subsequent emissions involve the less-volatile and more reactive components. In addition, not all emissions are initiated by the most volatile components. An indefinite amount of spillage occurs during handling; this spillage may be treated on a 1:1 basis the same as solvents (everything is assumed to be emitted into the atmosphere).

Eccleston (1970) evaluated total evaporative losses of leaded and prototype unleaded gasoline. Using U.S. Bureau of Mines reactivity factors, he estimated a 12 percent increase in photochemical reactivity for premium grade and about 28 percent increase for regular grade, in going from a typical leaded to a prototype unleaded gasoline.

c. Waste Combustion Emissions - In Table II-3, waste incineration and agricultural burning were ranked according to the overall "high" reactivity factor calculated from the data of the California Air Resources Board. This factor indicated that 11 percent of all waste combustion emissions are highly reactive.

From an analysis of the emission factors reported for the various waste combustion modes, the high reactivity factor of 11 percent appears to be significantly low. When the emission factors for unsaturated hydrocarbons and aldehydes are combined to estimate the reactive fraction of total emissions, the percentage of reactive emissions ranges from about 20 percent for industrial incineration to about 40 percent for domestic incineration.

Open burning, the principal disposal mode for all solid wastes, results in emissions that are about 27 percent reactive. Agricultural waste disposal emissions, which are almost entirely open burned, are thus estimated as being 27 percent reactive. Municipal, domestic (both urban and rural), and industrial wastes have been weighted according to their combustion modes to give an estimated average of 30 percent reactive emissions.

Based on these factors, high reactivity emissions from the major waste disposal categories of solid waste burning and agricultural burning are thus increased to 13.5 million, and 11.3 million tons/year, respectively.

d. Summary Source Ranking - In summary, the best estimate of source ranking according to photochemical reactivity is given in Table II-4. This ranking represents the relative source contributions to photochemical smog on a national basis. Because of the very pronounced variations in smog potential with regional geographic and meteorological conditions, such national estimates may not show a true picture. The regional parameters affecting smog formation are discussed in the following subsection.

3. Regional Factors Affecting Photochemical Smog

Significant to the discussion of source ranking by photochemical reactivity is some consideration of the regional differences that affect photochemical smog formation and its adverse effects.

Even though considerable study may yet be required to elucidate completely the mechanism of photochemical smog formation, experts tend to agree that certain atmospheric conditions are necessary for significant photochemical smog formation. These necessary conditions are generally given as:

1) presence of reactive organics (above some threshold value)

2) presence of nitrogen oxides in sufficient quantity to initiate photochemical reaction

3) a stagnant or poorly ventilated atmosphere to trap and retain reactants

4) intense sunlight

The existence and level of photochemical smog is generally monitored by total oxidant concentration which in-

Table II-4 - "Best Estimate" Reactivity Ranking of Major Emission Sources

Source Category	Total Hydrocarbon Emissions 10^6 tons/yr	"High Reactivity" Emissions 10^6 tons/yr
Solvent Evaporation	7.1	1.9
Solid Waste Combustion (urban, domestic, commercial, and industrial)	4.5	1.4
Agricultural Waste Combustion	4.2	1.1
Petroleum Products Storage and Marketing	2.3	1.0
Petroleum Production and Refining	1.9	0.2
Chemical Process Industry	1.4	negligible
Other Industrial Processes	∿1	negligible
Fuel Combustion	0.4	negligible
Coal Refuse Burning	0.2	not estimated
Forest Wildfires	2.4-3.0	not estimated
Totals	25.4-26.0	5.6

cludes not only ozone, but other photochemical oxidants such as peroxyacetyl nitrate (PAN) and organic peroxides. Most of the recent literature on episodic distribution of smog is based on the 1968 California standard for ambient air quality of 0.15 ppm oxidant for one hour by the neutral KI method. The recent and more stringent national ambient air standard for photochemical oxidant has not been considered in our treatment of geographic distribution, but would greatly increase the number of so-called smog days for the various affected regions.

Historically, California has been most affected by photochemical smog, primarily because of the meteorological conditions which predominate over much of the state during the late summer and early fall months. These meteorological conditions fulfill the third and fourth requirements listed above for the formation of smog, namely stagnation and strong sunlight. In recent years, however, the increased levels of reactant precursors over other metropolitan areas of the U.S. have resulted in almost all parts of the country being affected at least occasionally by adverse smog levels.

Holzworth (1967, 1969) analyzed the meteorological factors relating limited dispersion to smog potential for various regions of the United States. He showed that the episodic nature of limited atmospheric dispersion can be assessed in terms of morning and afternoon mixing heights and averaged wind velocities through the mixing layers.

After defining an episode of limited dispersion as no mixing height greater than 1500 meters, no average wind speed greater than 4.0 m/sec, and no precipitation, all for at least 2 days, Holzworth used this definition in an analysis of the five year weather data for four stations. In 5 years, the total of such episode-days were as follows: Oakland, California, >200; Washington, D.C. and Denver, Colorado, ∿40; St. Cloud, Minnesota, 3. To be truly indicative of photochemical smog potential, these weather data on dispersion trends should be combined with solar irradiation data, but they do, however, show the general trend across the U.S.

Faith (1968) reported that analysis of ambient air monitoring data on oxidant concentration indicated the following trend in annual frequency of smog days (oxidant exceeding 0.15 ppm for 1 hr): Los Angeles Basin, 200 days; San Francisco Bay Area, 50 days; Denver, 14 days; St. Louis, 7 days; Cincinnati, 5 days; Washington, D.C., 4 days; Chicago, none. The California Air Resources Board

(1969), using the same oxidant level criterion, have reported the following smog day frequencies (days/year) for California air basins in 1968: Los Angeles, 206; San Francisco, 67; San Diego, 95.

Studies conducted in both Los Angeles and San Francisco have shown that measured ambient oxidant levels are quite dependent on geographic location of sampling stations within an air basin. For example, Sandberg et al (1971) reported oxidant concentration trends for the 8 monitoring stations in the San Francisco Bay Area basin. The average high-hour oxidant concentrations follow the general off-shore flow of air, with the highest concentrations observed at Livermore, which is in a sheltered valley downwind of the central district. The 1969 average high-hour concentrations for days with comparable weather conditions show a four-fold range, from 0.04 ppm at San Francisco to 0.18 ppm at Livermore. This local variation within a particular air basin shows that the single station data available in many metropolitan areas may not be a true indication of maximum levels within that area.

Reported data indicate that regions outside of California are affected by order-of-magnitude lower smog problems than the major California air basins. More detailed studies, similar to those in San Francisco, are needed to show the true magnitude of the smog potential in any particular area.

D. VEGETATIVE DAMAGE

The secondary pollutants resulting from photochemical reactions produce the greatest amount of vegetative damage by air pollutants in specific areas. Of the primary hydrocarbon air pollutants, only ethylene has been found to produce significant vegetative damage.

Ethylene emitted by industrial processes and by fuel and waste combustion acts as a growth modifier on a wide variety of plants. Its greatest economic impact results from damage to citrus fruit and ornamental and cut flowers. Exposure to ethylene concentrations as low as 0.1 ppm for a few hours have resulted in sepal damage to sensitive flowering species.

Smog products, principally ozone and peroxyacetyl nitrate (PAN), have extensively damaged trees and crops in the smog affected areas of California. Recent estimates of crop losses from air pollutant damage in California, (Anon., 1971), show that smog products and ethylene are responsible for most of the total damage. The individual pollutants and their estimated percentage contribution to total crop damage are:

Ozone - 50%
PAN - 18%
Fluorides - 15%
Ethylene - 14%
SO_2 - 2%
Particulates - 1%

Weidensaul and LaCasse (1970) presented results of a statewide survey of air pollutant damage to vegetation in Pennsylvania. Although their data are not representative of annual pollutant damage, the survey results showed significant losses from oxidant exposure damage.

E. MATERIALS DAMAGE

Materials damage by hydrocarbon pollution is not well documented. The most often mentioned adverse effects are those of photochemical oxidants on rubber and plastics resulting in cracking and loss of elasticity. Other effects noted have been discoloration and deterioration of architectural coatings, and the formation of resistive coatings on electrical contacts resulting from polymerization of organic air pollutant species.

Only crude estimates of total materials damage costs have been reported. Wohlers and Feldstein (1965), for example, estimated economic effects of smog products in the Bay Area. Total yearly costs in materials damage to fabrics, rubber, paint and electrical contact points was estimated at $15 million.

CHAPTER II

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III. MAJOR SOURCES AND THEIR EMISSIONS

A. INTRODUCTION

The development of the ranking of pollutants and sources given in the preceding section required the identification, definition, and detailed analysis of hydrocarbon emissions from the major stationary sources. In the initial stages of the study, criteria and guidelines were developed which limited the study to significant areas; these criteria and guidelines were, however, broad enough to allow inclusion of source categories not considered in the preliminary screening selection.

The major source categories treated in this chapter are shown in Table III-1. This table serves not only as a summary of estimated total hydrocarbon emissions from the various sources but also as an index to the chapter contents.

The major literature sources utilized for this portion of the study were the trade magazines and general technical literature, as well as the reports of related government-sponsored contracts. Additional input was obtained from questionnaire surveys of pollution control agencies and trade associations. These latter data sources were of limited utility, but did provide some input in specific areas. Discussion and analysis of the questionnaire surveys are presented in Appendix G.

The general approach to the review of each of the major source categories was to define, where possible, the total amounts of material processed and to apply published emission factors for the calculation or estimation of hydrocarbon emissions. Because of the qualitative and sometimes contradictory nature of much of the literature information, rather broad assumptions were made to arrive at emission estimates. These assumptions are defined and, where possible, documented with actual examples.

With some few exceptions, data from the foreign literature were not utilized primarily because of a lack of information on the similarity of foreign practices with those used in the United States. Since differences in raw materials, processing steps, and types of control in prac-

Table III-1 - Summary of Major Source Hydrocarbon Emissions

Major Source	Secondary Source	Total Hydrocarbon Emissions 10^5 tons/yr	Page Reference
Coal Combustion			III-7
	Electric Utilities	0.43	
	Industrial	0.46	
	Domestic and Commercial	0.26	
Natural Gas Combustion			III-9
	Electric Utilities	0.10	
	Industrial	0.36	
	Commercial and Institutional	0.21	
	Domestic	0.24	
Fuel Oil Combustion			III-10
	Electric Utilities	0.33	
	Industrial	0.15	
	Commercial and Institutional	0.15	
	Domestic	0.62	
Wood Combustion			III-11
	Industrial	0.17	
	Domestic	0.83	
Coal Refuse Combustion		2.0	III-16
Agricultural Burning			III-17
	Field and Crop Residue	25.0	
	Controlled Timber and Land Clearance	17.0	
Forest Wildfires		24.0-30.0	III-18
Industrial Solid Waste Combustion			III-19

Table III-1 (continued)

Major Source	Secondary Source	Total Hydrocarbon Emissions 10^5 tons/yr	Reference
	Major Manufacturing	3.0	
	Miscellaneous Manufacturing and Commercial	7.0	
	Lumbering	7.0	
	Construction and Demolition	5.0	
	Food Processing and Marketing	5.0	
Municipal and Domestic Solid Waste Combustion			III-23
	Urban Collected	7.0	
	Urban Uncollected	4.0	
	Rural Collected	4.0	
	Rural Uncollected	3.0	
Crude Oil Production		2.2	III-33
Petroleum Refining			III-39
	Crude Storage at Refineries	3.2	
	Crude Storage in Transportation System	4.7	
	Gasoline Storage at Refineries	4.2	
	Refinery Operations	8.3	
Petroleum Product Marketing			III-46
	Gasoline Storage	7.8	
	Other Distillate Storage	2.9	
	Gasoline Transfers	12.0	
	Other Distillate Transfers	1.0	
Organic Solvent Usage			III-54

Table III-1 (continued)

Major Source	Secondary Source	Total Hydrocarbon Emissions 10^5 tons/yr	Page Reference
	Surface Coatings	30.0-40.0	
	Degreasing	6.5-9.5	
	Dry Cleaning	2.5-4.0	
	Printing and Publishing	1.8-2.3	
	Rubber and Plastics	6.0-7.5	
	Other Solvent Usage (unidentified sources)	8.1-24.6	
Chemical Process Industry		14.0	III-67
Specific Industrial Processes			
	Carbon Black	3.0	III-71
	Coke Ovens	2.0	III-73
	Pulp and Paper (Kraft, Softwood only)	0.5	III-79
	Phthalic Anhydride	0.1-0.4	III-82
	Rubber and Plastics (vinyl chloride, butadiene and acrylonitrile only)	0.4	III-83

tice have a direct bearing on the resultant emissions, the survey was generally limited to literature directly pertaining to sources in the United States.

B. FUEL COMBUSTION

Stationary fuel combustion sources are represented by the wide variety of furnaces and boilers used to convert fuel to heat energy. These include steam-electric utility boilers, industrial and commercial process boilers and space heaters, and domestic space heaters. The major fuels used by such sources are coal, oil and natural gas. These fossil fuels currently supply nearly 95 percent of the United States energy requirements. Other fuels consumed are wood, lignite, liquified petroleum gases, coke, refinery gas, and other by-product gases, but the usage of these fuels is relatively minor compared with coal, oil, and natural gas.

The gross energy consumption by major fuel types and consuming sectors are shown in Table III-2.

In the review of the literature, it was found that use of wood for fuel, although relatively minor from a total energy consideration, does contribute significant amounts of hydrocarbons to the atmosphere. Thus, estimates of wood fuel consumption and the resulting emissions were made.

Reported studies of flue gas and combustion product analysis from actual combustion sources which have considered organic emissions have generally been limited to the measurement of "total hydrocarbon", generally by flame ionization methods. In a few reported studies, aldehydes and organic acids are measured separately by other methods.

Flame ionization methods theoretically detect any volatile C-H bonded species and thus can measure low molecular weight aldehydes and acids. In practice, differences in sampling methods, e.g. heated or unheated sample probes, result in significant variation in the amounts of less volatile species being detected.

Where emission factors for "total hydrocarbons" and "aldehydes" or "organic acids" have been reported, these have been combined to arrive at total hydrocarbon emissions. Thus, our combined values may result in some

Table III-2 - Summary of Fuel Consumption - 1968 Stationary Sources (a)

	Coal (b)		Petroleum (c)		Natural Gas	
Source	10^{12} BTU	10^{6} tons	10^{12} BTU	10^{6} bbl	10^{12} BTU	10^{9} ft^{3}
Electric Utilities	7,130	296.8	1,181	214.4	3,245	3,144
Industrial	5,616	191.6	4,474	812.0	9,258	8,971
Household and Commercial	586	19.9	6,581	1,194.4	6,451	6,251
Miscellaneous and Unaccounted	1	0.1	295	53.5	---	---

(a) data from U.S. Bureau of Mines and Federal Power Commission.

(b) includes bituminous, lignite and anthracite.

(c) includes liquefied refinery gases and natural gas liquids, values converted to equivalent bbl basis.

indeterminate amount of double counting. This double counting is felt to be minor in view of the overall uncertainty of the reported emission factors.

1. Coal Combustion

Coal, more particularly bituminous coal, is our most abundant fossil fuel. However, localization of natural deposits coupled with transportation costs has limited its significant usage to about two thirds of the nation, predominantly in the central and eastern sections.

Emissions from coal combustion have been reviewed and summarized by several authors. Smith (1966) covered the available literature through about 1965. More recent summaries have been presented by Duprey (1968) and McGraw and Duprey (1971). These reviewers evaluated published data and arrived at representative emission factors for typical coal burning installations.

For large coal-burning power plants, the most complete study of emissions is that reported by Cuffe et al (1964, 1965), in which several types of full-scale installations were tested under both normal and partial load conditions. Their measured emissions of total gaseous hydrocarbons and total aldehydes are in reasonable agreement with estimates obtained by using the emission factors of McGraw and Duprey (1971). However, in tests on one boiler, Cuffe et al measured total organic acid emissions, both before and after fly ash collection (electrostatic). The average value for five tests, after fly ash collection, was 224 ppm by volume (dry basis), as acetic acid. Converting this value to lb/ton of coal gives 11.8 lb/ton. This value for organic acids appears to be unusually high and, for this study, is considered only insofar as it emphasizes the need for further analytical studies.

For the estimate of emissions made in this present study, the emission factors for coal combustion given by McGraw and Duprey (1971) were felt to be a reasonable concensus of the literature data. These emission factors are given in Table II-3 below.

Table III-3 - Uncontrolled Emission Factors for Bituminous Coal (lb/ton of coal burned)

(10^6 BTU/hr heat input)	Hydrocarbons (as CH_4)	Aldehydes (as HCHO)
Greater than 100 (utility and large industrial boilers)	0.3	0.005
10 to 100 (large commercial and general industrial boilers)	1	0.005
Less than 10 (commercial and domestic furnaces)		
Stoker	3	0.005
Hand fired	20	0.005

For domestic and commercial usage, the decreasing usage of hand fired furnaces led us to choose the factor for stoker fired units as being more representative of total emissions from this source category.

Coal consumption data by various sectors of the economy are given by the Bureau of Mines (1969) and for steam-electric utilities by the Federal Power Commission (1968). For the calculation of emissions from coal burning utilities, we chose to use the data from the Federal Power Commission. These data cover some 528 steam-electric plants which comprise 92 percent of total capacity and 96 percent of the power generation in the contiguous United States.

The distribution of coal consumption by industrial and domestic and commercial users is given for 1968 by the United States Bureau of Mines (1969).

These data and the emission factors of McGraw and Duprey (1971) were used to derive total organic emissions by state and consuming sector. These detailed breakdowns of coal consumption and emissions are given in Appendix H.

2. Natural Gas Combustion

Natural gas has long been considered a clean-burning, or relatively non-polluting, fuel. However, much of this reasoning has been based on the absence of the particulate and SO_x problems associated with coal and fuel oil and has not taken into consideration the unburned or partially oxidized organic emissions from gas combustion.

Only a few studies have been made of trace organic emissions from natural gas combustion. McGraw and Duprey (1971) reviewed available data and reported emission factors for hydrocarbons (as CH_4), aldehydes, and organics. The factors given by McGraw for hydrocarbons appear to be unusually high when compared with emission factors reported for other fuels.

Chass (1960) reported the results of extensive source testing of both gas and oil burning sources in Los Angeles County. Gaseous hydrocarbon emissions were not reported for either gas or oil combustion because the concentrations "were below the range of the analytical technique". However, Chass does not describe the analytical technique used.

Magill and Benoliel (1952) summarized in one brief table the emissions from all types of oil and gas burning equipment. Converting their emission factor for organic emissions from gas combustion from lb/ton to lb/MMcf gives an emission factor of about 75 lb/MMcf. Since this number is a lumped factor for all types of sources and since Smith (1962) rejected their similar number for fuel oil emissions, for this study these particular data were discounted.

For the estimates of emissions from natural gas combustion in this study, we chose to use the emission factors for total hydrocarbons used by the Bay Area Air Pollution Control District (1969) and the factors for aldehyde emissions given by McGraw and Duprey (1971). These selected emission factors are shown in Table III-4.

Table III-4 - Emission Factors for Natural Gas Combustion (lb/MMcf burned)

Source	Total Hydrocarbons	Aldehydes
Utility Boilers	4	3
Industrial Process Boilers	7	3
Domestic and Commercial Heating Units	1	10

The consumption of natural gas by various sectors of the economy was taken from U.S. Bureau of Mines data (1969). Breakdowns of natural gas consumption and hydrocarbon emissions by state and consuming sector are given in Appendix H.

3. Fuel Oil Combustion

The various petroleum fractions used for fuel combustion are generally described by the NBS Commercial Standards for Fuel Oils (Johnson and Auth, 1951). Grades 1 and 2 are distillate oils of sufficient volatility to allow usage in general purpose burners not equipped with preheaters. Grades 4 through 6 are residual oils used for industrial and utility burners equipped with preheating facilities. Additionally, some kerosene is used for heating purposes.

The emissions from fuel oil combustion have been reviewed by Smith (1962), Duprey (1968), and McGraw and Duprey (1971). The emission factors selected for this study were those of McGraw and Duprey and are shown in Table III-5.

Data on the consumption of fuel oils and kerosene were obtained from the U.S. Bureau of Mines (1970). Emissions from the usage of kerosene for space heating were not broken down by state, but rather a total nationwide estimate was made, using the emission factors for domestic distillate fuel oil combustion.

Table III-5 - Emission Factors for Fuel Oil Combustion (lb/1000 gallons burned)

Source	Total Hydrocarbons	Aldehydes
Utility Boilers	5	1
Industrial and Commercial Boilers		
Residual -	3	1
Distillate -	3	2
Domestic	3	2

4. Wood Combustion

Wood is no longer a major fuel for industrial heat or power generation, however, in those industries where considerable quantities of wood wastes are generated, it is used as fuel to a limited extent. According to the Environmental Engineering (1970) report on the wood pulping industry, the consumption of wood wastes, primarily bark and chips, for fuel amounted to about 15 million tons for 1968, at an estimated fuel value of 4500 BTU/lb. Industrial usage of wood for fuel by the furniture, plywood, veneer and other lumber industries was estimated by MSAR to be about 2 million tons.

The total industrial usage of wood and wood wastes for fuel was estimated at 17 million tons. Based on the emissions reported for wood and bark combustion in boilers of 2 lb/ton (McGraw, 1970), total hydrocarbon emissions from this source category total 34 million pounds, or 17 x 10^3 tons.

The usage of wood as domestic fuel is primarily limited to rural areas where other fuels are not readily available or are too expensive. The remaining domestic usage may be considered as recreational or esthetic usage of wood in fireplaces.

An estimated breakdown of wood fuel usage was given by Schurr and Netschert (1960), citing data from Stanford Research Institute. These data, shown in Table III-6, give actual consumption in 1950 and an extrapolated forecast for 1975.

Table III-6 - Fuel Wood Consumption (in units of 10^6 cords)

Year	heat, rural farm	heat, rural non-farm	heat, urban	Fireplace	Other	Total
1950	20.6	13.0	5.8	14.0	1.6	55.0
1975	2.3	3.7	2.4	17.0	0.2	[illegible]

More recent wood fuel consumption data are [illegible] in Statistical Abstract of the United States, 1969 (U.S. Bureau of the Census, 1969). This latter source gives 1962 consumption of wood for fuel as 1.124 billion cubic feet. At an average density of 40 lb/ft^3, this is equivalent to 22.5 million tons, or about 18 million cords. Thus, it can be seen that the Stanford forecast of 25.6 million cords for 1975 is considerably too high. We estimate current total domestic consumption of wood as fuel as being about 15 million tons/yr, primarily in fireplaces.

Assuming the hydrocarbon emission factor for fireplace and domestic fuel usage of wood to be similar to that for incineration of wood in conical burners, the average emission factor for such use is 11 lb/ton (McGraw and Duprey [1971]). Based on this emission factor, total emissions amount to about 82.5 x 10^3 tons from domestic usage of wood for fuel.

5. Polycyclic Aromatic Hydrocarbon Emissions

Studies conducted by the U.S. Public Health Service, as reported by Hangebrauck et al (1967), have shown fuel combustion sources to be significant contributors of polycyclic aromatic hydrocarbon (PAH) emissions to the atmosphere. These PAH emissions are almost entirely associated with the particulate emissions from combustion sources and are directly related to the combustion efficiency of the combustion source.

From measurements of total benzene soluble organic matter and chromatographic analyses for specific compounds, particularly benzo-a-pyrene (BaP), Hangebrauck derived estimates of emission factors for BaP from various heat generation sources. Based on these emission factors and Bureau of Mines data (1969) on fuel usage, current estimates of BaP emissions were derived, as shown in Table III-7.

For wood fuel usage, Hangebrauck's data on BaP emissions from single-chamber incineration of cardboard and wood packing crates were used to derive the average emission factor for wood combustion of 106 mg/ton for use with our estimated wood consumption.

6. Summary of Emissions

The data sources and emission factors described in the previous sections were used to derive a state-by-state breakdown of hydrocarbon and aldehyde emissions from fuel combustion. This breakdown is given in Table III-8.

Table III-7 - Estimated BaP Emissions from Fuel Combustion

Fuel Burned	1968 Usage (10^{12} BTU)	Emission Factor ($\mu g/10^6$ BTU)	Annual Emissions (tons)
Coal			
Utilities	7,074	90	0.7
Industrial	5,536	2,700	16.5
*Commercial	221	5,000	1.0
Residential			
Stoker	98	44,000	5.0
Handfired	128	1,400,000	197
Oil	12,531	200	2.8
Gas	18,954	100	2.1
Wood	32 x 10^6 tons	106 mg/ton	3.8

*U.S. Bureau of Mines total retail deliveries for 1968 distributed among commercial and residential usage according to Hangebrauck's (1967) relative distribution.

Table III-8 - Regional and State Breakdown of Fuel Combustion Emissions for 1968 (tons/year)

Region and State	Coal		Fuel Oil		Natural Gas		Totals	
	Total Hydrocarbons	Aldehydes	Total Hydrocarbons	Aldehydes	Total Hydrocarbons	Aldehydes	Total Hydrocarbons	Aldehydes
New England								
Maine	242	---	1,357	585	8	29	3,868	1,776
New Hampshire			807	388				
Vermont			379	229				
Rhode Island			1,050	466	25	79		
Connecticut	562	7	4,076	1,510	72	212	4,710	1,729
Massachusetts	750	8	9,265	3,767	136	543	10,151	4,318
Middle Atlantic								
New York	5,567	50	15,433	6,526	739	2,496	21,739	9,072
New Jersey	1,205	15	8,884	3,544	370	981	10,459	4,540
Pennsylvania	9,447	88	6,854	2,912	1,295	2,346	17,596	5,346
East North Central								
Ohio	14,960	116	1,558	895	1,545	3,587	18,063	4,598
Indiana	7,862	73	1,860	1,036	923	1,389	10,645	2,498
Illinois	13,318	99	3,333	1,656	1,584	3,432	18,235	5,187
Michigan	9,842	75	2,255	1,327	1,096	2,540	13,193	3,942
Wisconsin	6,347	35	1,468	919	512	849	8,327	1,803
West North Central								
Minnesota	2,387	15	1,363	770	477	980	4,227	1,765
Iowa	1,709	13	517	324	466	870	2,692	1,207
Missouri	2,303	24	652	355	486	1,270	3,441	1,649
North Dakota	1,049	9	271	166	17	75	1,534	467
South Dakota			170	103	27	114		
Nebraska	316	3	171	97	276	594	1,760	1,843
Kansas			172	71	825	1,078		
South Atlantic								
Delaware	1,982	25	571	247	45	62	5,889	2,103
Maryland			1,801	816	186	604		
Washington, D.C.	301	3	1,003	346				
Virginia	4,631	34	2,005	790	183	405	6,819	1,229
West Virginia	5,344	48	200	86	345	509	5,889	643
North Carolina	4,356	48	1,265	670	234	318	5,855	1,036
South Carolina	1,266	9	631	280	307	282	2,194	571
Georgia	2,335	31	776	315	580	831	8,756	2,773
Florida			4,483	1,106	582	490		
East South Central								
Kentucky	3,992	40	220	122	238	637	4,450	799
Tennessee	4,228	41	208	121	461	604	4,897	766
Alabama	3,298	42	189	66	667	709	4,878	1,414
Mississippi			128	65	596	532		
West South Central								
Arkansas	78	---	59	20	678	790	13,786	10,075
Louisiana			225	123	3,677	2,406		
Oklahoma			94	49	769	988		
Texas			631	301	7,575	5,398		
Mountain								
Colorado	526	8	116	71	298	397	1,074	614
Idaho	1,136	9	221	102	411	795	1,768	906
Montana	635	1	261	164	92	101	1,258	553
Nevada + Arizona	---	---	67	41	67	97	---	---
New Mexico	14	---	35	21	348	463	397	484
Utah	430	2	550	197	220	330	1,200	529
Wyoming	476	6	271	148	134	174	881	328
Pacific								
Alaska	374	2	279	150	12	39	665	191
California	24	---	3,563	1,025	3,608	5,365	7,195	6,390
Oregon	368	1	859	456	193	193	3,110	1,726
Washington			1,342	724	348	352		
Sub total, United States	113,660	980	84,110	36,353	33,831	47,537	231,601	84,870
Wood Combustion, total United States							99,500	---
Undistributed Kerosene Usage, total United States							5,432	3,275
Total United States							336,533	88,145

More detailed treatment of the individual consuming sectors, by region and state, is presented in Appendix H.

C. Solid Waste Combustion

1. Introduction

The dimensions and nature of the problems associated with solid waste disposal have attained national recognition during the past ten years, with many articles and reports having been published in an effort to define these problem areas. A dearth of quantitative data relegates many of these publications to general descriptions which contribute little toward our understanding of the total situation.

Many of those studies conducted in sufficient detail to arrive at reasonably quantitative estimates of waste generation and disposal have been directed toward urban or municipal areas, with little attention being paid to non-urban problems. This limitation has been necessitated for two principal reasons. One, the rapidly accelerating nature of urban refuse generation and its resultant effect on the major portion of the nation's population have combined to direct the highest priority to urban needs. Two, it is only in large urban areas that sufficient records are maintained to allow even semi-quantitative estimates of generation and disposal.

The widely dispersed and varied nature of the non-urban waste sources, such as agriculture, mining, and rural industrial operations, has prevented descriptions and measurement in any terms except crude estimates or extrapolations from limited data.

The most recent and well-documented study of waste generation and disposal on a national scale is the National Solid Wastes Survey. The survey results, as summarized by Black et al (1968), when combined with conservative estimates of waste generated by other sectors lead to a total national waste generation estimate of over 3.5 billion tons per year.

Other, perhaps less conservative, estimates of wastes from mineral and agricultural sources (for example, Business Week, 1970) would place our total national waste generation in the range of from 4 to 5 billion tons per year. An approximate breakdown of total waste generation is given in Table III-9.

For this study, development of estimates of hydrocarbon emissions from disposal of solid wastes required (1) estimation of the fractions of waste burned by the various combustion modes, i.e., municipal, industrial and commercial and domestic incineration and open burning, and (2) estimation of hydrocarbon emission factors most representative for these combustion modes.

Table III-9 - Approximate Breakdown of Total Solid Wastes Generation (MSAR estimate)

Source Category	Wastes Generated 10^9 tons/yr
Municipal, commercial and domestic wastes	0.3
Agricultural refuse (crop & field residues)	0.6
Animal wastes	1.5-2.0
Industrial wastes	0.6
Mineral wastes	1.0-1.5
Total	4.0-5.0

2. Solid Waste Sources

An assessment of hydrocarbon emissions from solid waste combustion requires the development of a system codifying the amounts of disposal methods of the solid wastes produced by various source categories.

Four categories were chosen for the initial subdivision in this systematized profile. These included: a) mining or mineral production; b) agricultural operations; c) industrial and commercial operations; d) municipal and domestic sources.

a. Mining Wastes

Solid wastes generated during mining operations include overburden, rejected material from cleaning and refining, and construction wastes. Although a large amount of waste is thus generated, much of it is innocuous in terms of air pollution problems. Notable exceptions are the open burning of construction and land clearance wastes and the combustion of coal refuse piles. Estimates of amounts of construction and clearance wastes burned were assumed to be lumped with the estimates of other similar wastes considered in the industrial and commercial wastes category.

Coal refuse burning has been reviewed by Sussman and Mulhern (1964) and Hall (1962). The main source of combustible refuse from coal mining derives from mechanical cleaning operations. U.S. Bureau of Mines (1968) statistics show that about 80 percent of total bituminous coal production was cleaned, generating 97 million tons of refuse, or about 18 percent of the total production.

The Nationwide Inventory of Air Pollutant Emissions, 1968 (U.S. Department of Health, Education and Welfare, 1970 estimated that coal refuse banks totalling 19 billion cubic feet were burning in 1964. GCA Technology (1970) cites an unpublished Bureau of Mines study which reported the total number of burning coal refuse banks in 1969 at 292, with a total volume of 7.3 billion cubic feet and containing an estimated equivalent of 18 million tons of coal. Sussman (1964) cites a Bureau of Mines estimate of 488 burning refuse banks. These figures would indicate significant progress in efforts to extinguish and prevent coal refuse combustion.

The highly variable nature of this combustion source makes any estimate of emissions highly questionable. Based on the GCA technology reported value of the equivalent of 18 million tons of coal burning in refuse banks and the emission factor for hand fired domestic coal furnaces of 20 lb/ton (McGraw & Duprey, 1971), the total hydrocarbon emissions are estimated at about 0.2 million tons/yr.

b. Agricultural Wastes

Solid wastes generated by agricultural sources include animal wastes, field crop residues, wastes from processing raw agricultural products, and land clearing debris. Total estimates of agricultural wastes vary widely. Environmental Science and Technology (1970) reported an estimated 2 billion tons/year of animal wastes alone. Black et al (1968) reported an estimated 550 million tons of agricultural waste and crop residue and approximately 1.5 billion tons of animal wastes. Business Week (1970) gave a total of 2.3 billion tons/year of agricultural wastes, with no breakdown given.

For our study, the amount of waste burned was of primary interest. Thus, animal wastes were ignored, since these are generally handled by field spreading and landfill disposal methods rather than by burning.

The major emissions of organic air pollutants result from open burning of field residues and vegetation for weed control and land clearance. Estimates of the total extent of such burning were derived by extrapolation of data reported for the San Francisco Bay Area by Johnson and James (1970). Thus, field and crop residues burned would total nearly 250 million tons/year on a national basis. Extrapolated estimates of wastes produced by land clearance would contribute an additional 35 million tons/year.

The agricultural waste estimates derived above are similar to totals reported in other studies. The Nationwide Inventory of Air Pollutant Emissions, 1968, gave an estimated total of nearly 280 million tons of crop residues, brush, weeds and other vegetation burned annually. GCA Technology (1970) gave a breakdown of open burning in which the agricultural wastes burned annually totalled 275 million tons.

Prescribed burning of timber and logging debris is widely practiced in several areas. For example, Bovee et al (1970) report that 200,000 acres of logging slash are burned annually in western Oregon and Washington. U.S. Forest Service Statistics for 1966, reported in the Nationwide Inventory of Air Pollutant Emissions 1968, indicated that controlled burning of timber lands covered some 3.5 million acres and represented about 76 million tons of combustible material. More recent estimates given by Wadleigh (1968) indicate a lower figure of 52 million tons burned by prescribed burning of logging debris and vegetation.

Forest wildfires contribute significant amounts of organic emissions annually. The combination of heterogeneous, wet fuel and insufficient oxygen combine to release total organic emissions which can exceed those from other open burning sources.

Forest Service statistics reported in the Statistical Abstract of the United States, 1969 and in the Annual Fire Report for the National Forests, 1968 show that, for the period from 1966 through 1968, an average of 4.5 million acres of forest land is burned annually by uncontrolled wildfires. Combining this acreage with the factor of 32 tons of combustible material per acre derived from the Nationwide Inventory (USDHEW, 1970) yields an estimate of 144 million tons of vegetation consumed by wildfires. Consideration of annual variation in acreage burned indicates that this latter figure may range from about 120 to 150 million tons per year.

In summary, agricultural wastes burned annually are estimated as: crop and field residues, 250 million tons; land clearance, 35 million tons; prescribed forest burning, 50 million tons. Forest wildfires, treated separately, result in an estimated annual burning of from 120 to 150 million tons of vegetation and logging residues.

c. Industrial and Commercial Wastes

Estimates of industrial and commercial waste generation vary widely and have been found to be, in many instances, unrealistically low. Again, this is primarily due to surveys and studies directed toward municipal or urban generation and collection. Our estimates of waste generation by the various sectors of industrial and commercial operations are based on an analysis of the waste generation factors for various industrial categories reported by Combustion Engineering (1969), GCA Technology (1970), and the University of California (1970), supplemented by other literature data where applicable.

To arrive at meaningful estimates, we have chosen to separate the industrial and commercial operations into five groups, primarily on the basis of their different waste generation characteristics. These groups are: major manufacturing; miscellaneous manufacturing and commercial; forestry related industries; demolition and construction; and food processing and marketing.

Major Manufacturing - Waste generation factors in pounds or tons per employee year for the major manufacturing industries have been reported by Combustion Engineering (1969) and the University of California (1970). These waste generation factors are based on total solid wastes generated, both combustible and non-combustible.

Excluding those industries treated separately, the employment statistics for nineteen SIC groups were combined with the waste generation factors to estimate the total solid wastes generated. Significant differences in the waste generation factors reported resulted in estimates of total wastes generated ranging from 48 to 96 million tons/year. For our selected value, we have taken the average or about 72 million tons/year.

The breakdown of major manufacturing categories and their estimated total solid waste generation is given in Table III-10.

Estimates of the disposition or disposal mode for industrial wastes vary widely. This variation is due not only to the widely differing types of wastes being generated and disposed, but to the lack of clear definition of terms used by the various investigators and reporting sources. We have assumed that the fraction of wastes being disposed by burning, either by incineration or open burning, is composed totally of combustible waste. This assumption is an oversimplification which could result in our estimates being somewhat high, since wastes burned often include variable amounts of non-combustible material.

Based on their survey of community collection practices, Black et al estimated that from 30 to 40 percent of generated industrial waste is self disposed. Combustion Engineering (1969), from their survey of industry groups, reported that about 50 percent is handled on-site by the generator, 25 percent disposed off-site by the generator, and about 21 percent by contract disposal, with only 3 percent going to municipal collectors. Much of the off-site disposal, however, ends up in municipally owned disposal sites.

As to ultimate disposal mode, Combustion Engineering (1969) estimated that incineration and open burning combined account for from 30 to 40 percent of the total waste disposed. For this study, 25 percent open burned and 10 percent incinerated were selected as being more realistic in view of our assumption that wastes burned are totally combustible.

Miscellaneous Manufacturing and Commercial - Using an average waste generation factor for representative industries of 3.25 tons per employee year (Combustion Engineering, 1969), the total solid waste generated by miscellaneous, commercial, and government sources was estimated to be about 150 million tons/year.

Table II-10 - Major Manfuacturing Solid Waste Generation

Industry Group	1968 Employment (1,000)	Waste Generation Factors (tons/employee/yr) (a)	(b)	Total Solid Wastes Generated (10^6 tons/yr) (a)	(b)
Ordnance	342	1.45	0.66	0.50	0.23
Furniture	474	wood 5.75			
		metal 8.55	20.16	2.37	9.56
Stone, clay & glass	638	2.65	18.11	1.69	11.55
Primary metal	1,301	1.50	6.73	1.95	8.76
Fabricated metal	1,389	1.45	6.73	2.01	9.35
Machinery	1,958	1.45	4.18	2.84	8.18
Electrical Equipment	1,963	1.05	2.98	2.06	5.85
Transportation Equipment	2,026	1.10	3.39	2.23	6.87
Instruments	451	2.65	2.52	1.20	1.14
Tobacco	86	5.40	2.49	0.46	0.21
Textile Mills	985	1.25	0.53	1.23	0.52
Apparel	1,417	0.30	0.53	0.43	0.75
Paper & Allied	698	8.75	12.54	6.11	8.75
Printing & Publishing	1,063	8.25	13.20	8.77	14.03
Chemicals (except paint)	1,032	6.30	8.21	6.50	8.47
Rubber & Plastics	558	5.95	1.55	3.32	0.86
Leather	357	9.70	2.49	3.46	0.89
Petroleum Refining	151	6.30*	----	0.95	
Paint	70	2.65	----	0.19	
Total	16,959			48.27	95.97

*Estimated as same as chemicals

(a) From Combustion Engineering (1969)
(b) From University of California (1970)

Ultimate disposition was assumed to be similar to that of the major manufacturing industries, i.e. 10 percent incinerated and 25 percent open burned.

Forestry-Related Industries - The lumbering and forestry-related industries - saw mills, planing mills, etc. generate exceptionally large amounts of solid wastes. Combustion Engineering (1969) reported a waste generation factor of 277 thousand lb per employee year. For the 1968 national employment of 602,000 persons, this results in estimated generation of 83 million tons.

Sawmill wastes disposal was estimated by Combustion Engineering to be over 75 percent burned in conical or tepee burners. We have assumed ultimate disposal of all wastes from forestry-related industries to be 65 percent conical burning and 10 percent open burning.

Construction and Demolition Wastes - Contract construction and demolition is another special category distinguished by high waste generation factors. Combustion Engineering gave a factor for construction waste generation of 87 thousand lb/employee year. A similar generation factor of 82.5 thousand lb/employee year was given by the University of California. For demolition, the waste generation factor given by Combustion Engineering was over 4.5 million lb/employee year. Based on 1968 census data for total employment, the total waste generated by construction and demolition was estimated to be about 140 million tons/year.

Ultimate disposition modes have not been reported, but traditionally, open burning has been used for combustible wastes. We assumed 25 percent disposal by open burning.

Food Processing and Marketing - Reported estimates of food processing wastes have been limited to surveys of canning and preserving, dairy products processing, and meat packing. Waste generation factors for these industries range from 3 to 5 tons per employee year. Combustion Engineering (1969) reported supermarkets as being especially high in waste generation at nearly 18 tons/employee year.

A review of other literature sources indicated that total waste generation should be considerably higher than the 35 to 40 million tons/year derived from the above generation factors.

Mercer (1963) cited typical waste production figures for fruit and vegetable processing in California. Solid wastes generated ranged from 7 to over 15 percent of the total tonnage of fruits and vegetables processed.

Shearon (1952), in discussing citrus fruit processing, gave a figure of 60 percent wastage in juice production, Hickey (1966) gave amounts of "special wastes" in the San Francisco Bay Area. About 10 percent of these "special wastes" were derived from cannery operations.

If a 10 percent wastage factor is applied to all fruit, vegetable, meat, fish, poultry and dairy products processed per year, the solid wastes generated could range as high as 200 million tons per year. For this study, we took a conservative estimate of 100 million tons per year for all wastes from food processing and marketing.

Ultimate disposition was assumed similar to that for the manufacturing industries and commercial operations, or 10 percent incinerated and 25 percent open burned.

d. Municipal and Domestic Wastes

Urbanization and industrialization have served to increase both the generation of solid wastes and the difficulties of disposal for most communities. With nearly 75 percent of the population in urban environments, municipal wastes are a dominant factor in urban governmental problems.

Although they represent only a small fraction of the total solid wastes, municipal wastes have been given paramount attention in technical surveys and investigations because of the social and economic problems associated with urban waste disposal. This public and governmental concern has encouraged and supported studies to determine the various aspects of the problem and to provide quantitative data.

Niessen et al (1970), Kaiser (1967), and Rogus (1963) were used as general references for municipal wastes generation and disposal practices. Combustion Engineering (1969) and the National Emissions Standards Study (1970) provided data for the location and capacity of municipal incineration. The National Solid Wastes Survey provided recent estimates of waste generation and disposition derived from community collection practices.

Urban or municipal waste generation factors generally include not only household and municipal wastes, but significant amounts of industrial and commercial wastes. Thus, in our treatment, some unavoidable overlap or double counting may have occurred, even though attempts were made to minimize this. By comparison, however, uncertainties in the total estimates of generating segments obviates the significance of any double counting that may have occurred.

Waste generation factors given by Niessen (1970) and urban population were used to derive state-by-state estimates of municipal solid waste generation. These generation factors are heavily weighted by data on wastes collected for municipal disposal and include unstated amounts of commercial and industrial wastes as well as household or domestic wastes. As given in Appendix I, this breakdown also provides estimates of municipal incineration and municipal open burning. These latter estimates were derived by assuming municipal incineration at 50 percent of reported capacities and open burning of urban wastes at 20 to 25 percent, except in states that prohibit open burning. Where specific data were made available as a result of our questionnaire survey of pollution control agencies, exceptions to the above methods were made.

Totalling the state-by-state estimates indicates that U.S. municipal waste generation amounts to about 170 million tons/year.

The National Solid Wastes Survey (Black et al, 1968) indicated that collected wastes averaged 5.32 lb/person day on a national basis, as shown in Table III-11. These data reflect only the amount collected. Black et al estimated the total generation of both collected and uncollected wastes at 10 lb/person day, with industrial wastes accounting for 3 lb/person day and household, commercial and municipal wastes (street & alley, etc.) accounting for 7 lb/person day. By excluding industrial and construction demolition wastes from these per capita estimates, we arrived at the estimates of urban and rural waste generation and disposal shown in Table III-12. Urban population was assumed to be 73 percent of total population.

Table III-11 - Average Solid Waste Collected (pounds per person per day)

Waste	Urban	Rural	National
Household	1.26	0.72	1.14
Commercial	0.46	0.11	0.38
Combined*	2.63	2.60	2.63
Industrial	0.65	0.37	0.59
Demolition, Construction	0.23	0.02	0.18
Street & Alley	0.11	0.03	0.09
Miscellaneous	0.38	0.08	0.31
Totals	5.72	3.93	5.32

*Combined household and commercial wastes from collections that could not be characterized separately.

Table III-12 - Household & Municipal Waste Generation and Disposal (10^6 tons/year)

Source	Generated	Incinerated	Open Burned
Urban collected	129	13	32
Urban uncollected	34	3	17
Rural collected	35	4	18
Rural uncollected	30	--	15
Totals	228	20	82

Municipal incineration of urban collected wastes was assumed to amount to 50 percent of stated capacity for all incineration capacity listed by Niessen (1970) and the National Emission Standard Study. Ten percent of uncollected urban wastes were assumed to be incinerated in domestic incinerators. Ten percent of rural collected wastes were assumed to be incinerated municipally. Open burning was assumed to be the disposal method for 25 percent of urban collected wastes and 50 percent of all other urban and rural wastes, both collected and uncollected.

3. Waste Combustion Emissions

In order to estimate the organic air pollutant emissions from the combustion of solid wastes as categorized above, emission factors were selected as being representative of the various combustion modes and types of wastes burned.

A general review of published studies of waste combustion emissions showed an extremely wide range of experimental results, depending on the analytical techniques employed and combustion parameters. Wide variations are not unexpected since reproducible and representative combustion conditions are difficult to achieve with such heterogeneous mixtures as are represented by the various waste mixtures. Even under the best conditions,such as those with a modern multiple chamber incinerator, variations in waste composition, moisture content, and combustion air can significantly affect the type, amount, and composition of organic emissions.

For the estimates obtained in this study, the reported emissions and emission factors were analyzed and combined to give reasonably representative averages of total organic gas emissions. Thus, our selected emission factors may be somewhat higher than those reported on the basis of only total hydrocarbon as determined by flame ionization. Several investigators, namely Feldstein (1963), Darley (1966), Gerstle and Kemnitz (1967), and Boubel (1968), reported analyses for emission components such as organic acids, aldehydes or total oxygenates, and unsaturated hydrocarbons, as well as total hydrocarbons. Special weight was given these more detailed analyses in deriving our selected factors for estimating total organic emissions.

Unfortunately, the failure of many investigators to give sufficient detail about analytical techniques and combustion conditions does not allow valid assessment of their results. We attempted to give greater weight to those studies which were obtained under field conditions. Even so, an uncertainty of at least a factor of two exists in the selected values.

The selected emission factors, in terms of total organic emissions, are shown in Table III-13. In Appendix

I, the reported data from which the selected emission factors were derived are detailed.*

Table III-13 - Estimated Emission Factors for Solid Waste Combustion Sources

Combustion Mode	Total Organic Emissions (lb/ton burned)
Incineration	
Municipal	4
Industrial and Commercial	14
Conical Burners (wood)	20
Domestic	40
Open Burning	
Municipal	45
Industrial and Commercial	30
Lumbering	30
Field & Crop	20
Land Clearance	40
Demolition & Construction	30
Coal Refuse	20
Forest Wildfires	40

The highest emissions, and also the widest variation in reported values, result from domestic single chamber incinerators and open burning sources. Again, only a few investigators have determined anything other than gaseous hydrocarbons, generally by flame ionization analysis. Feldstein (1963) in a reworking of Yocom and Hein (1956) data on single chamber domestic incinerators reported the highest values found. These data, also used by BAAPCD in their

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*To illustrate the selection of representative emission factors for waste combustion, the factor of 4 lb/ton of waste burned by municipal incineration was derived from full-scale incinerator test data reported by Niessen (1970). These data show a range of total hydrocarbon emissions of from 0.9 to 6.3 lb/ton (average = 1.84±2.16) and aldehydes of from 0.001 to 0.84 lb/ton. The factor of 4 lb/ton was selected as an upper mid-range value from these data.

1969 inventory, show total organic emissions to be about 250 lb/ton, with 24 lb/ton of organic acids and 25 lb/ton of aldehydes. These data were derived from burning a 50/50 mixture of grass clippings and paper, a perhaps unrealistic mixture for any except domestic backyard burning.

Gerstle & Kemnitz (1967) reported results for simulated open burning of municipal refuse, landscape refuse, and auto components. For both municipal and landscapes refuse they report about 50 lb/ton of gaseous hydrocarbons (as CH_4) and about 15 lb/ton of organic acids (as CH_3COOH). Reported aldehyde concentrations were low, from 0.005 to 0.01 lb/ton. Gerstle and Kemnitz also reported that limited chromatographic analyses indicated that the gaseous hydrocarbons consisted of 30 to 40 percent unsaturated hydrocarbons.

For domestic incineration, which may range from fairly well controlled installations with a primary air supply to poorly controlled burning cans and baskets with insufficient combustion air, we chose to use an intermediate factor of 40 lb/ton for the total organic emissions. Of the 40 lb/ton total, we estimated that combined aldehydes and organic acids account for 10 to 15 lb/ton.

The wide variety of wastes burned by open burning and the variation in emission factors reported do not justify attempting to estimate separate emission factors for each source category; however, some general distinctions may be made.

For open burning of municipal and domestic refuse, we selected the values given by Gerstle and Kemnitz as being reasonable mid-range values. Thus, for this source category, we chose a factor of 45 lb/ton for total organic emissions, of which about 15 lb/ton are from combined acids and aldehydes.

For industrial wastes not otherwise specified, an emission factor of 30 lb/ton for total organic gases was assumed for all open burning.

For agricultural burning and forest wild fires, where the combustible materials may range from dry grass and crop stubble to green brush and trees, we have chosen to use two different values. For field crop and residues, an emission factor of 20 lb/ton was selected for total organic emissions. This value is heavily weighted by the midrange values reported by Darley (1966) and Boubel (1969) for total gaseous hydrocarbons.

For land clearance and forest fires, a higher factor of 40 lb/ton for total organic emissions was selected. This value was weighted by the high values reported by Darley and Boubel for green vegetation.

4. Summary

The estimated solid waste generation and disposal by combustion for the various source categories are summarized in Table III-14. Application of the selected emission factors from Table III-13 to the amounts burned results in the estimated total hydrocarbon emissions shown in Table III-15.

D. PETROLEUM PRODUCTION, REFINING AND MARKETING

1. General

The processing of crude oil into salable products and the marketing of these products constitute a significant potential source of hydrocarbon emissions. Some hydrocarbon losses occur during the production of crude oil; however, these losses are small compared with those from refining and marketing.

The magnitude of the petroleum industry may be illustrated by some statistics for 1968 taken from the 1971 International Petroleum Encyclopedia and the 1968 Minerals Yearbook. Domestic production of crude oil in 1968 was 9 million bbl daily from almost 554,000 wells. Total U.S. refining capacity was approximately 13 million bbl/day with an average refinery throughput averaging nearly 11 million bbl/day. Total U.S. consumption of petroleum products amount to nearly 14 million bbl/day, with motor gasoline alone accounting for nearly 5.9 million bbl/day.

2. Industry Description

Input crude from the field is treated to remove sediment which can be removed by sedimentation or settling. In some cases, crude oil and water are in the form of an emulsion that must be treated to achieve separation. Heat and chemicals are used to break the emulsion and free the oil. Gas-oil separators are employed to strip the liquid crude of gaseous hydrocarbons.

Table III-14 - Summary of Waste Generation and Combustion

Source Category	Total Waste Generated (10^6 tons/yr)	Total Waste Burned: Incineration (10^6 tons/yr)	Total Waste Burned: Open Burning (10^6 tons/yr)
Mining Coal Refuse	97	---	18
Agriculture	7550	---	
Crop and Field Residues			250
Controlled Timber and Land Clearance			85
Forest Wild Fires	---	---	120-150
Industrial			
Major Manufacturing	72	7.2	18
Miscellaneous Manufacturing and Commercial	150	15	37.5
Forestry and Lumbering	83		62.3
Construction and Demolition	140		35
Food Processing and Marketing	100	10	25
Municipal & Domestic			
Urban Collections	129	13	32
Urban Uncollected	34	3	17
Rural Collections	35	4	18
Rural Uncollected	30	---	15

Table III-15 - Summary of Estimated Organic Emissions From Solid Waste Combustion Sources

Source Category	Total Organic Emission (10^6 tons/year)
Mining (Coal Refuse Only)	0.2
Agriculture	
Field & Crop Residues	2.5
Controlled Timber & Land Clearance	1.7
Total	4.2
Forest Wildfires	2.4-3.0
Industrial	
Major Manufacturing	0.3
Miscellaneous Manufacturing and Commercial	0.7
Lumbering	0.7
Construction & Demolition	0.5
Food Processing & Marketing	0.5
Total	2.7
Municipal and Domestic	
Urban Collected	0.7
Urban Uncollected	0.4
Rural Collected	0.4
Rural Uncollected	0.3
Total	1.8
Grand Total	11.3-11.9

A transportation system consisting of pipelines, tankers, barges, tank cars, and tank trucks move the crude petroleum to the refineries for processing. Refineries received 75.8 percent of their crude oil supply by pipeline, 23.0 percent by water, and 1.2 percent by tank cars and tank trucks in 1968.

Operations at a modern refinery are highly complex, but in general consist of four major steps: separation, conversion, blending, and treating. These steps are made up of a number of unit operations, which include distillation, catalytic conversion, polymerization, and isomerization. The products resulting from these operations are blended and treated to give the desired end products. Because of the variable market demand for particular fractions and products, a high degree of flexibility in processing is required.

Included at the refinery plant are innumerable equipment-technique combinations which supply the service necessary to maintain the continuity of the total refining process. Equipment-technique combinations pertinent to this study include: condensers, cooling towers, boilers and heaters, compressors, oil-water separators, air blowing, pipeline valves and flanges, and pipeline blinds.

Although all of the above primary and secondary processes and equipment contribute to total hydrocarbon losses, the most significant refinery losses result from the necessary use of vast storage facilities. As a rule, refineries maintain about two barrels of storage capacity for each barrel of inventory. The National Petroleum Council (1963) suggests that this surplus storage factor (2.0 in 1963) is the minimum amount of storage required to maintain necessary flexibility in the refining process. Evaporative loss from storage tanks is the greatest contributor to hydrocarbon emissions.

The role of the refinery in the marketing of its products is dependent upon the definition. Distinct separation of refining operations and marketing cannot be readily made because of multiple usage of facilities.

The modern refinery serves as the first link in the marketing and distribution chain. The bulk of all refinery products are turned into pipelines, tankers, or barges and transported to large holding facilities or bulk terminals. From these, gasoline and other products are routed to the consumer either directly or through smaller bulk stations and service stations. These bulk terminals and stations may be refinery owned and operated or may be independent of the refinery. Storage and transfer operations at each point along the distribution chain are potential emission sources.

In order to simplify the estimation of hydrocarbon emissions from the petroleum industry, generalizations and assumptions were made of the flow of crude oil and refined products through a hypothetical "typical" production, refining, and marketing operation. Figure III-1 shows schematically the distribution path and the major emission points treated in subsequent portions of this section. By assuming total industry crude and product flow through this hypothetical path, total industry hydrocarbon emissions were derived.

Subsequent discussions treat each of the major emission points along the distribution path of Figure III-1.

3. Crude Petroleum Production

Approximately 70% of U.S. crude oil is produced in the states of and offshore of Texas, Louisiana, and California. Domestic production of crude in 1968 totalled 3,329,042,000 barrels from almost 554,000 wells, as reported by Bureau of Mines (1968).

Data on crude petroleum production emissions are sparse. Emission inventories of Los Angeles County (California Air Resources Board, 1969) indicate hydrocarbon emissions of 60 tons/day from crude production, versus 50 tons/day from refining and 110 tons/day from marketing. A breakdown of crude production source emissions given in a pollution study of Monterey and Santa Cruz Counties, California (Monterey-Santa Cruz County Unified APCD, 1968) is shown in Table III-16. These losses resulted from an annual production of 18.5 million barrels of crude oil.

By assuming these crude production emissions to be typical of total U.S. practice, extrapolated emissions for the total U.S. crude production of 3.33 billion barrels yields estimated annual crude production emissions of about 224,000 tons.

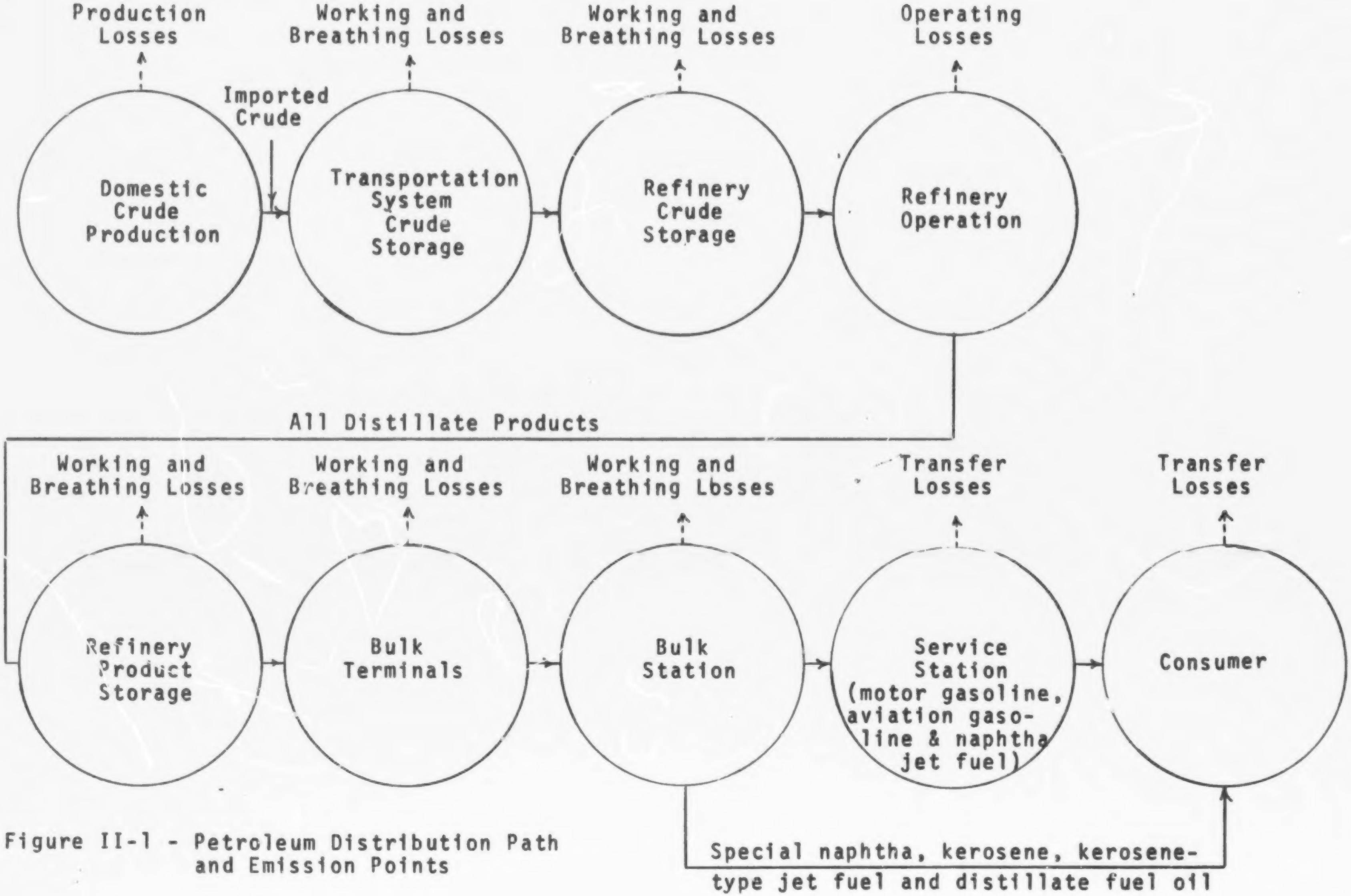
Production Losses
Working and Breathing Losses
Working and Breathing Losses
Operating Losses
Imported Crude
Domestic Crude Production
Transportation System Crude Storage
Refinery Crude Storage
Refinery Operation
All Distillate Products
Working and Breathing Losses
Working and Breathing Losses
Working and Breathing Losses
Transfer Losses
Transfer Losses
Refinery Product Storage
Bulk Terminals
Bulk Station
Service Station (motor gasoline, aviation gasoline & naphtha jet fuel)
Consumer
Special naphtha, kerosene, kerosene-type jet fuel and distillate fuel oil

Figure II-1 - Petroleum Distribution Path and Emission Points

4. Crude Storage in Transportation System

Crude oil is supplied to refineries through a transportation system which includes tank farms, bulk terminals, and other storage points outside of the refinery. In order to estimate storage emissions from this crude transportation system, all of the crude delivered to the refinery is assumed to have passed through available storage tankage facilities enroute to the refinery.

Recommended methods for estimation of losses from storage tanks have been given in a series of bulletins prepared by the Evaporation Loss Committee of the American Petroleum Institute. Most useful for estimating storage losses are Bulletin 2513 (1959), Bulletin 2517 (1962), and Bulletin 2518 (1962). In order to use these methods of loss calculations, values must be assigned for such factors as total storage tankage, specific tank sizes and ranges, throughput rate, and meteorological conditions.

The National Petroleum Council (1963) reported that storage capacity outside the refinery in 1960 was about 274 million barrels. Assuming storage capacity to be proportional to refinery capacity, extrapolation of the 1960 storage data to 1968 refinery capacity (U.S. Bureau of Mines, 1968) yields an estimate of crude storage capacity outside of the refinery in 1968 of about 304 million barrels.

Estimated storage tank emissions are divided into two categories; breathing losses and working losses. Breathing losses result from vapor expansion and contraction due to atmospheric temperature changes and are influenced by the vapor pressure of the stored liquid, tank coating reflectivity, and ambient temperature changes. Working losses result from escape of vapors during tank filling operations and are significantly affected by the number of filling operations or turnovers. The turnover rate is obtained from the ratio of total annual throughput to tank capacity.

Storage tank emissions are also a function of tank roof construction. Floating roof tanks are widely used to reduce emissions over those from cone or fixed roof tanks. For this study, the percentage distribution of floating roof and fixed roof tanks was that given by Duprey (1968) as being typical of industry practice: 75 percent floating roof and 25 percent fixed roof.

Table III-16 - Estimated Crude Oil Production Emissions, Monterey County, 1967 (Crude Production of 18.5 Million Barrels)

Point Source	Emissions, tons/day Hydrocarbons	Emissions, tons/day Other Organic Gases
Storage Tanks	0.1	
Boilers and Heaters		
Gas		0.1
Oil		0.5
Waste Water Separators	0.2	
Pumps	1.9	
Compressors	0.1	
Relief Valves	0.2	
Pipeline Valves	0.3	

Rather than assuming all storage losses to occur from a single, average tank size, we chose to distribute the loss calculations over a range of tank sizes felt to be typical of industry practice. A Poisson distribution function was thus used to generate the number of tanks of incremental sizes over a range from 20 to 160 thousand barrel capacity. For crude oil storage outside the refinery, the generating function was induced to peak at an assumed average tank size of 80,000 barrel capacity.

The advantages of using a tank size distribution are two-fold. First, it results in more realistic emissions since emissions vary as a power function of the tank diameter and hence the use of a single average tank size would not necessarily yield average total emissions. Second, the range of tank sizes allows for the application of a range in the paint and roof factors used in the loss calculations. It was assumed that the larger tanks were newer and more carefully maintained than the smaller tanks.

Meteorological conditions, temperature, and windspeed were taken from the API Bulletins and adjusted to reflect average crude storage conditions.

The turnover rate (annual throughput/tank capacity) for estimation of the working losses was estimated at 13, from the annual throughput of 3.8 billion barrels and the estimated storage capacity outside the refinery of 304 million barrels.

Tank outage, or the amount of vapor space above the stored liquid is difficult to estimate. API Bulletin 2518 gives outage in feet for tank test data used in developing loss correlation methods but does not give total tank height. We assumed a typical outage of 50 percent of tank height.

The Reid vapor pressure, used to estimate the true vapor pressure of the liquid under storage conditions, was estimated from data presented in API Bulletin 2518. Crude oil Reid vapor pressures range from about 3 to over 10 lb; a value of 7.5 lb was adopted as being typical.

Estimated hydrocarbon emissions from crude oil storage in the transportation system are tabulated in Table III-17. Hydrocarbon emissions from this source of crude storage totalled 470,000 tons.

Table III-17 - Crude Losses in the Transportation System

Storage Conditions	Tank Size (10^3 bbl)	Tank Size Distribution (%)	Distributed(1) Capacity (10^6 bbl)	Number(2) of Tanks	Specific Throughput(3) (10^3 bbl/tank)	Paint(4) Factor	Roof & (5) Paint Factor	Control(6) Factor (%)	Working Loss (10^3 bbl)	Breathing Loss (10^3 bbl)	Control(6) Factor (%)	Standing Storage Loss (10^3 bbl)
Crude oil Total storage capacity,	20	8	24.3	1,215	260	1.3	3.2	25	78.9	91.1	75	175.0
304 x 10^6 bbl	40	15	45.5	1,142	520	1.2	2.8	25	112.8	171.3	75	239.8
Liquid Temp, 55°F	60	20	60.7	1,011	780	1.2	2.8	25	146.6	227.5	75	297.2
Temp Change, 17°F	80	20	60.7	758	1,040	1.2	2.5	25	144.0	231.2	75	249.0
Reid V.P., 7.5 lb	100	15	45.5	455	1,300	1.2	2.2	25	102.4	170.6	75	157.7
True V.P., 5.2 psia	120	10	30.4	253	1,560	1.1	2.2	25	66.4	113.9	75	96.0
Wind Speed, 9 mph	140	7	21.2	151	1,820	1.1	1.3	25	43.4	77.8	75	38.3
Turnovers, 13	160	5	15.2	95	2,080	1.0	1.0	25	27.3	52.3	75	19.6
SUBTOTALS									721.8	1,135.7		1,272.6

Total Crude Loss

Volume - 3.130 x 10^6 bbl

Weight - 470 x 10^3 tons (at 300 lb/bbl)

(1) Percent distribution x total storage capacity
(2) Total capacity ÷ specific tank volume
(3) Specific tank volume x turnovers
(4) Paint factors from API Bulletin 2518
(5) Paint and roof factors from API Bulletin 2517
(6) Percentage of tanks with fixed or floating roof

5. Refinery Emissions

Hydrocarbon emissions from the refineries were estimated by combining the activity of all refineries into a composite or single process. This was followed by application of suggested emission factors for each source point. A number of assumptions and judgments were made to fill existing data voids. In some cases the accepted basis for a judgment was a single data "point". Major hydrocarbon sources are discussed separately and are preceded by a discussion which outlines the mechanism of the tabulation and the guidelines used. The refinery storage area is treated in greater detail because of its importance.

Reported emission factors for refinery operation are based primarily on a detailed study of refinery operations conducted in the Los Angeles Area and reported in Public Health Service Publication 763 (1960). These have been summarized by Duprey (1968) and are shown in Table III-18. For many of the point sources, ranges of emission factors are given, reflecting both uncontrolled and controlled operations.

A highly questionable aspect in any estimation of total emissions is the extent of control in application. Comparison of community survey data from areas other than Los Angeles indicates a range of total refinery emissions of from less than 0.1 percent of crude throughput to nearly 0.3 percent. These data are listed in Table III-19. The variations shown for total refinery emissions in these survey estimates may not represent any meaningful geographical or chronological trend but may simply reflect differences in estimating procedures.

a. Refinery Storage Emissions

In this study estimates of hydrocarbon emissions from storage areas at refineries are limited to those from crude oil and gasoline storage. Losses of other distillates during storage are detailed in the later section on Petroleum Product Marketing (Section III D-6).

Storage tank losses at the refineries were treated in a similar fashion to that described previously for crude oil storage losses in the transportation system. To use the API recommendations for storage loss calculation, values were assigned for such factors as total storage tankage, specific tank sizes and ranges, throughput and turnover rates, and meteorological conditions.

Table III-18 - Hydrocarbon Emission Factors for the Petroleum Industry(1)

CRUDE STORAGE	
Fixed Roof	
Breathing Loss -	0.3 lb/day/1000 gal storage capacity
Working Loss -	8.0 lb/1000 gal throughput
Floating Roof	
Breathing Loss -	30-160 lb/day/tank
DISTILLATE STORAGE	
Fixed Roof (vapor pressure >1.5 psia)	
Breathing Loss -	0.4 lb/day/1000 gal storage capacity
Working Loss -	11 lb/1000 gal throughput
Floating Roof (vapor pressure >1.5 psia)	
Standing Storage -	4.8 lb/day/1000 bbl storage capacity
Fixed Roof (vapor pressure <1.5 psia)	
Standing Storage -	1.7 lb/day/1000 bbl storage capacity(2)
Floating Roof (vapor pressure <1.5 psia)	
Standing Storage -	1.6 lb/day/1000 bbl storage capacity(2)
BOILERS AND PROCESS HEATERS -	140 lb/1000 bbl oil burned 0.03 lb/1000 ft^3 gas burned
FLUID CATALYTIC CRACK UNITS -	220 lb/1000 bbl fresh feed
MOVING-BED CATALYTIC CRACK UNIT -	87 lb/1000 bbl fresh feed
COMPRESSOR ENGINES -	1.2 lb/1000 ft^3 gas burned
BLOWDOWN SYSTEM -	5-300 lb/1000 bbl refinery capacity

Table III-18 (continued)

PROCESS DRAINS -	8-210 lb/1000 bbl waste water
VACUUM JETS -	0-130 lb/1000 bbl vacuum distillation
COOLING TOWER -	6 lb/10^6 gal cooling water
MISCELLANEOUS LOSSES -	lb/1000 bbl refinery capacity
Pipeline Valves & Flanges -	28 lb/1000 bbl refinery capacity
Vessel Relief Valves -	11 lb/1000 bbl refinery capacity
Pump Seals -	17 lb/1000 bbl refinery capacity
Compressor Seals -	5 lb/bbl refinery capacity
Others, (Direct Blowing, Sampling, etc.) -	10 lb/1000 bbl refinery capacity

(1) Duprey (1968)
(2) Public Health Service Publication 763

Table III-19 - Refinery Emissions Reported by Community Surveys

Region	Date	No. of Refineries	Estimated total Refinery Capacity	Hydrocarbon Emissions tons/yr	% Weight Loss
Seattle-Tacoma	1963(a)	4	201,800	9,651	0.087
St. Louis, Mo.	1967-1968(b)	4	362,000	32,170	0.16
Erie County, N.Y.	1967(c)	1	37,000	3,200	0.16
		1	42,000	6,300	0.28
San Francisco	1969(d)	5	477,000	19,037*	0.07(+)*
Louisville, Ky.	1969(e)	1	22,000	2,300	0.19
	TOTAL		1,141,000 bbl/cd	72,658 tons/yr	

*Does not include distillate storage.

(a) Seattle-Tacoma Air Pollutant Emission Inventory, 1963.

(b) St. Louis Air Pollutant Emission Inventory, 1968.

(c) National Emission Standard Study, Report of the Secretary of HEW to the United States Congress, March, 1970.

(d) Source Inventory of Air Pollutant Emissions, San Francisco Bay Area, 1969.

(e) Louisville Metropolitan Area Air Pollutant Emission Inventory, 1969.

The 1963 report of the National Petroleum Council listed storage tankage at refineries for the 1962-1963 period. Extrapolating these data to 1968 refining capacity data (U.S. Bureau of Mines, 1968) results in an estimate of crude storage capacity at refineries of 137 million barrels. Similarly, estimated gasoline storage is 204 million barrels.

Establishment of typical tank sizes and ranges poses a major problem. Data from the Los Angeles study (U.S. Public Health Service Publication 763, 1960) lead to average tank capacities of 55,000 barrels for crude oil and about 28,000 barrels for distillate. Private communications from knowledgeable petroleum industry personnel indicate that, for a medium-sized refinery on the East Coast, crude tanks average about 150,000 barrels and distillate tanks about 80,000 barrels.

For our study, a Poisson distribution function was used to generate the number of tanks of incremental sizes over a range felt to be representative of refinery practice. For crude oil storage, the generating function covered the range from 20 to 160 thousand bbl and was induced to peak at 80,000 bbl. For distillate storage the range was from 20 to 120 thousand bbl with the peak at 60,000 bbl.

Data on meteorological conditions, including temperature and wind speed, were taken from API Bulletin 2513 and adjusted to reflect the predominance of warm coastal regions as refinery locations.

API data (Bulletin 2518) suggest that the working loss is essentially independent of the turnover rate (throughput/tank capacity) for turnover rates of less than 36 per year. The ratio of annual throughput to capacity gave turnover rates of about 30 for crude oil and about 10 for gasoline.

Tank outage was assumed to be 50 percent of tank height. Reid vapor pressure was taken as 10.5 lb for gasoline (U.S. Bureau of Mines, 1971) and as 7.5 lb for crude oil.

The distribution of floating and fixed roof tanks was assumed to be 75 percent floating roof and 25 percent fixed roof (Duprey, 1968).

Hydrocarbon emissions from refinery storage of crude oil and gasoline are tabulated in Table III-20 and 21. For 1968, the total estimated hydrocarbon emissions are: refinery crude oil storage, 324,000 tons; refinery gasoline storage, 424,000 tons.

Table III-20 - Crude Storage Losses at Refineries

Storage Conditions	Tank Size (10^3 bbl)	Tank Size Distribution (%)	Distributed[1] Capacity (10^6 bbl)	Number[2] of Tanks	Specific Throughput[3] (10^3 bbl/tank)	Paint[4] Factor	Roof &[5] Paint Factor	Fixed Roof Losses			Floating Roof Losses	
								Control[6] Factor (%)	Working Loss (10^3 bbl)	Breathing Loss (10^3 bbl)	Control[6] Factor (%)	Standing Storage Loss (10^3 bbl)
Crude oil total storage capacity, 137 x 10^6 bbl	20	8	11.0	550	600	1.20	2.8	25	36.4	104.5	75	86.6
	40	15	20.6	515	1,200	1.20	2.5	25	54.7	199.6	75	106.2
Liquid Temp, 70°F	60	20	27.4	457	1,800	1.16	2.2	25	70.3	260.5	75	116.9
Temp Change, 17°F	80	20	27.4	343	2,400	1.16	2.2	25	68.2	262.4	75	113.2
Reid V.P., 7.5 lb	100	15	20.6	206	3,000	1.044	1.3	25	45.8	196.2	75	45.3
True V.P., 5.7 psia	120	10	13.7	114	3,600	1.04	1.0	25	28.4	131.1	75	21.4
Wind Speed, 9 mph	140	7	9.6	69	4,200	1.04	0.9	25	20.4	93.2	75	13.1
Turnovers, 30	160	5	6.9	43	4,800	1.00	0.75	25	13.3	66.7	75	7.3
SUBTOTALS									337.5	1,314.2		510.0

Total Crude Loss

Volume - 2.162 x 10^6 bbl

Weight - 324 x 10^3 tons (at 300 lb/bbl)

(1) Percent distribution x total storage capacity
(2) Total capacity ÷ specific tank volume
(3) Specific tank volume x turnovers
(4) Paint factors from API Bulletin 2518
(5) Paint and roof factors from API Bulletin 2517
(6) Percentage of tanks with fixed or floating roof

Table III-21 - Gasoline Storage Loss at Refineries

								Fixed Roof Losses			Floating Roof Losses	
Storage Conditions	Tank Size (10^3 bbl)	Tank Size Distribution (%)	Distributed[1] Capacity (10^6 bbl)	Number[2] of Tanks	Specific Throughput[3] (10^3 bbl/tank)	Paint[4] Factor	Paint &[5] Roof Factor	Control[6] Factor (%)	Working Loss (10^3 bbl)	Breathing Loss (10^3 bbl)	Control[6] Factor (%)	Standing Storage Loss (10^3 bbl)
Gasoline	20	19	39.3	1,965	200	1.20	2.8	25	199.0	267.7	75	350.8
Total storage capacity, 204 x 10^6 bbl	40	22	45.7	1,143	400	1.20	2.5	25	244.3	257.2	75	289.3
Liquid Temp, 70°F	60	22	45.7	762	600	1.16	2.2	25	228.6	239.1	75	238.9
Temp Change, 17°F	80	17	34.3	429	800	1.16	2.2	25	171.6	183.4	75	177.0
Reid V.P., 10.5 lb	100	10	20.6	206	1,000	1.04	1.3	25	103.0	97.9	75	56.3
True V.P., 6.8 psia	120	9	18.4	153	1,200	1.00	1.0	25	93.7	81.1	75	36.8
Wind Speed, 9 mph												
Turnovers, 10												
SUBTOTALS									1,020.0	1,126.4		1,149.1

Total Gasoline Loss

Volume - 3.296 x 10^6 bbl

Weight - 424 x 10^3 tons (at 257 lb/bbl)

(1) Percent distribution x total storage capacity
(2) Total capacity ÷ specific tank volume
(3) Specific tank volume x turnovers
(4) Paint factors from API Bulletin 2518
(5) Paint and roof factors from API Bulletin 2517
(6) Percentage of tanks with fixed or floating roof

b. Emissions from Refinery Operations

Data for 1968 operating capacities (charge capacities) for the various refining operations (catalytic cracking, etc.) were obtained from the survey of operating refineries given in the Oil and Gas Journal (1968). These data were combined with the emission factors for refinery operations listed in Table III-18 to derive refinery emission estimates. Where ranges of emission factors are given, as for blowdown systems, process drains, and vacuum jets, midrange values were adopted as being typical. Where emission factors were not based on refinery capacities, estimates were derived from data given in Public Health Service Bulletin 763 and extrapolated to total U.S. production figures.

Estimated hydrocarbon emissions from the various refining operations are tabulated in Table III-22. Annual emissions from refining operation sources total 833,000 tons.

6. Petroleum Product Marketing Emissions

a. Product Distribution

Many refineries, in addition to normal refinery operations, serve as the first link in the marketing and distribution of products. Supplies for the local market and for shipment to smaller storage facilities leave the refinery by tank truck, car and barge. The bulk of all refinery products, however, are turned into pipelines and transported to large holding facilities (bulk terminals and bulk stations). Eventually gasoline is trucked from these sites to neighborhood service stations and then transferred to the automobile tank.

In the previous discussion of refinery emissions (Section III D-5), gasoline losses from refinery storage were treated. For convenience of calculation, all other refinery products are treated in this section by combining both refinery and non-refinery storage losses as product marketing losses. Gasoline marketing losses are treated subsequent to refinery storage.

b. Hydrocarbon Emissions

Estimates of hydrocarbon emissions during the marketing of refinery products were obtained in the following manner: first, the major refinery products were divided into gasoline-like and non-gasoline type, as shown in Table III-23.

Table III-22 - Hydrocarbon Emissions from Refinery Operations

Source Point	Emission Factor	Hydrocarbon Emissions (tons/yr)
Sewers and Separators	105 lb/1000 bbl refinery capacity	216,000
Catalytic Regenerators		
Fluid Bed	22 lb/1000 bbl fresh feed	143,000
Moving Bed	57 lb/1000 bbl fresh feed	10,000
Blowdowns-Turnarounds	120 lb/1000 bbl refinery capacity	243,000
Compressor Engines	1.2 lb/1000 ft^3 fuel gas	33,000
Boilers and Heaters	13.5 lb/1000 bbl refinery capacity	28,000
Pipeline Valves and Flanges	28 lb/1000 bbl refinery capacity	57,000
Vessel Relief Valves	11 lb/1000 bbl refinery capacity	22,000
Pump Seals	17 lb/1000 bbl refinery capacity	35,000
Compressor Seals	5 lb/1000 bbl refinery capacity	10,000
Others (Air Blowing, Blind Changing, and Sampling)	10 lb/1000 bbl refinery capacity	20,000
Cooling Towers		16,000*
Totals		833,000

*Estimated from Los Angeles Data (Public Health Service, 1960)

Table III-23 - Gasoline and Non-Gasoline Type Products

Gasoline Type	Non-Gasoline Type
Motor gasoline	Jet fuel (kerosene)
Aviation gasoline	Kerosene
Special naphthas	Distillate oils
Jet fuel (naphthas)	

Storage and transfer losses were tabulated for the more volatile or gasoline-like products. In general, it was assumed that products in this class were the same as motor gasoline, both in the number of transfers and in the magnitude of evaporative loss. Special naphthas which are not used as fuels were carried or routed only to the tank of the user. The evaporative and transfer losses for naphtha along this shorter route were assumed to be comparable to losses for gasoline.

Only storage losses were tabulated for the less volatile products. In general, these products consist of a variety of blends or mixtures and especially in the case of distilled oils undergo severe seasonal variations in stocks. Products of this type were classed as having vapor pressure less than 1.5 psia; the emission factors suggested by Public Health Service Publication No. 763 were employed.

Distillate Storage Losses - In the 1967 Census of Business (Bureau of the Census, 1970), the number, storage capacity and sales figures for bulk stations and terminals were given for various petroleum products. Petroleum bulk stations are defined as generally having capacities less than 2 million gallons and receive their supply by truck or rail transport. Bulk terminals are of larger capacity and are supplied primarily by pipeline, tanker,or barge.

Bulk terminal and bulk station storage capacity for gasoline is given as 171.7 million barrels. To obtain the total storage capacity for other distillates it was necessary to consider both refinery and non-refinery tankage. The 1967 Bureau of Census data detailed bulk storage tanks for each specific product. A similar breakdown of refinery storage of products such as the jet fuels, aviation gasoline, and special naphthas was not available. Total refinery storage capacity for these distillates was estimated by multiplying the available stock at refineries by the factor 2.0. The factor represents a reasonable approximation of the ratio of storage to inventory. The data obtained are shown in Table III-24.

To estimate evaporative and working losses of petroleum products from storage and transfer during marketing, we used the emission factors shown in Table III-18. The wide variety of tank sizes and storage conditions and the indeterminate turnover rates do not justify the more detailed loss treatment given to refinery storage losses of crude oil and gasoline. For this treatment, the distribution of floating and fixed roof tanks was considered to be the same as for refinery storage. The estimated emissions from bulk storage of the major petroleum products are summarized in Table III-25.

Emissions for non-refinery bulk storage of gasoline and total bulk storage of other petroleum products totals about 644,000 tons/year.

Transfer Losses - Transfer losses in the gasoline distributive chain occur during terminal loadings and during the loading of service or retail station tanks and automobile tanks. Losses resulting from transferring gasoline from storage to automobile tanks are as follows:

> Terminal loadings of 83 x 10^9 gallons with a loss factor of 6.4 lb/1000 gallons yield 266,000 tons.
>
> Service tank loadings of 83 x 10^9 gallons with a loss factor of 9.0 lb/1000 gallons yield 373,000 tons.
>
> Automobile tank loadings of 83 x 10^9 gallons with a loss factor of 12 lb/1000 gallons yield 498,000 tons.

Losses for these three steps total 1,137,000 tons. In all cases, loadings were assumed to be conducted under a 50-50 splash/submerged filling condition.

A reasonable approximation of transfer losses of other distillates was obtained similarly. Total loadings of each major distillate were based on the domestic demand of each product as reported by the U.S. Bureau of Mines (1968).

Table III-24 - Petroleum Product Storage Capacities (excluding motor gasoline)

Product	Refinery Storage(a) (10^6bbl)	Bulk Station& Terminal Storage (10^6bbl)	Total Est.Storage Capacities(b) (10^6bbl)
Aviation Gasoline	14.0	5.8	19.8
Special Naphtha	11.6	5.7	17.3
Jet Fuel (Naphtha)	17.8	17.4	23.9
Jet Fuel (Kerosene)	30.8		42.1
Kerosene	46.2	29.6	75.8
Distillate Fuel Oil	346.2	169.5	515.7

(a) Estimated as twice December 1968 stocks

(b) Refinery plus bulk storage

Table III-25 - Petroleum Product Storage Losses

Product	Emissions
Motor Gasoline	
Estimated storage capacity: 171.7 x 10^6 bbl (7.214 x 10^9 gal)[a]	
Throughput: 83 x 10^9 gal	
Loss Calculation	
Fixed Roof (25%)	
a) Breathing @ 0.4 lb/day/1000 gal storage capacity[b]	131,700 tons/yr
b) Working @ 11 lb/1000 gal throughput[b]	114,100 tons/yr
Floating Roof (75%)	
a) Standing storage @ 4.8 lb/day/1000 bbl storage capacity[a]	112,800 tons/yr
total	358,600
Aviation Gasoline	
Estimated storage capacity: 19.8 x 10^6 bbl (831.6 x 10^6 gal)	
Throughput: 1.28 x 10^9 gal (domestic demand)[c]	
Loss Calculation	
Fixed Roof (25%)	
a) Breathing @ 0.4 lb/day/1000 gal storage capacity[b]	15,200 tons/yr
b) Working @ 11 lb/1000 gal throughput[b]	1,800 tons/yr
Floating Roof (75%)	
a) Standing storage @ 4.8 lb/day/1000 bbl storage capacity[d]	13,000 tons/yr
total	30,000
Special Naphthas	
Estimated storage capacity: 17.3 x 10^6 bbl (726.6 x 10^6 gal)	
Throughput: 1.134 x 10^9 gal (domestic demand)[c]	

Table III-25 (continued)

Loss Calculation	
Fixed Roof (25%)	
a) Breathing @ 0.4 lb day/1000 gal/ storage capacity(b)	13,300 tons/yr
b) Working @ 11 lb/1000 gal throughput(b)	1,600 tons/yr
Floating Roof (75%)	
a) Standing storage @ 4.8 lb/day/ 1000 bbl storage capacity(a)	11,400 tons/yr
total	26,300
Jet Fuel (Naphtha)	
Estimated storage capacity: 23.9 x 10^6 bbl (1.00 x 10^9 gal)	
Throughput: 5.31 x 10^9 (domestic demand)(c)	
Loss Calculation	
Fixed Roof (25%)	
a) Breathing @ 0.4 lb/day/1000 gal storage capacity(b)	18,300 tons/yr
b) Working @ 11 lb/1000 gal throughput(b)	7,300 tons/yr
Floating Roof (75%)	
a) Standing storage @ 4.8 lb/day/ 1000 bbl storage capacity(a)	15,700 tons/yr
total	41,300
Jet Fuel (Kerosene)	
Estimated storage capacity: 42.1 x 10^6 bbl	
Loss Calculation	
Fixed Roof (25%) @ 1.7 lb/day/ 1000 bbl storage capacity(a)	3,300 tons/yr
Floating Roof (75%) @ 1.6 lb/ day/1000 bbl storage capacity(a)	9,200 tons/yr
total	12,500

Table III-25 (continued)

Kerosene	
Estimated storage capacity: 75.8 x 10^6 bbl	
Loss Calculation	
Fixed Roof (25%) @ 1.7 lb/day/ 1000 bbl storage capacity(a)	5,900 tons/yr
Floating Roof (75%) @ 1.6 lb/ day/1000 bbl storage capacity(a)	16,600 tons/yr
total	22,500
Distillate Oil	
Estimated storage capacity: 515.7 x 10^6 bbl	
Loss Calculation	
Fixed Roof (25%) @ 1.7 lb/day/ 1000 bbl storage capacity(a)	40,000 tons/yr
Floating Roof (75%) @ 1.6 lb/ day/1000 bbl storage capacity(a)	112,900 tons/yr
total	152,900
Total Product Storage Emissions, excluding refinery stored gasoline	644,100 tons/yr

(a) Bulk Stations and Terminals Only
(b) Duprey, 1968
(c) 1968 Minerals Yearbook, Bureau of Mines
(d) Public Health Publications No. 763

Estimated transfer losses for aviation gasoline totalled 17,400 tons and for naphtha-type jet fuel 72,200 tons. Loss of special naphtha, from the storage tank to the user's tank only, was estimated at 8,969 tons. Total estimated loss of all these products was 98,000 tons. These estimates were obtained by analogy to the transfer loss calculation for gasoline.

7. Summary of Petroleum Hydrocarbon Losses

Table III-26 summarizes the total hydrocarbon emissions within the petroleum industry. Total estimated emissions were about 4.2 million tons for 1968. The breakdown shows storage losses of 1.9 million tons and losses in transfer amounting to about 1.3 million tons. Process or refinery emissions totalled 0.8 million while about 0.2 x 10^6 tons were emitted during crude oil production.

Several potentially important emission sources were considered but not estimated because of a lack of data on which to base meaningful emission estimates. These included losses occurring during marine and pipeline transfers of crude oil and finished products, as well as accidental spills and pipeline leakage.

E. SOLVENT EVAPORATION

1. General

Since the pioneering studies of smog formation by Haagen-Smit et al (1950, 1952), organic solvent evaporation has been recognized as a significant source of air pollution. Lunche (1957) reported survey data which indicated that 50 percent of the stationary emissions of organics in the Los Angeles area in 1955-1956 were due to solvent evaporation sources. More recent data from San Francisco show that, even with the stringent controls applied, solvent emissions are the largest single category of stationary organic emissions, amounting to about 36 percent of the total stationary source organic emissions (Bay Area Air Pollution Control District, 1969).

The wide variety of solvents and end users makes a detailed inventory of usage and resulting emissions highly speculative. Additional complications arise from the fact that for many of the organic chemicals used as solvents, significant amounts of the total production are used in non-solvent applications. To arrive at total emissions estimates,

Table III-26 - 1968 Summary of Petroleum Industry Hydrocarbon Emissions

Operation	Emissions (tons/yr)
1. Crude Oil Production	224,000
2. Crude Storage in Transportation System	470,000
3. Crude Storage at Refinery	324,000
4. Refinery Operations	
Separators	216,000
Catalytic Cracking Regenerators	153,000
Blowdowns and Turnarounds	243,000
Compressors	33,000
Boilers and Heaters	28,000
Miscellaneous (valves, flanges, seals, blind changing, cooling towers, etc.)	160,000
Subtotal, Refinery Operations	833,000
5. Marketing	
Gasoline Storage	
Refinery	424,000
Bulk Stations and Terminals	358,600
Other Distillate Storage	
Aviation Gasoline	30,000
Jet Fuel (naphtha)	41,300
Jet Fuel (kerosene)	12,500
Special Naphtha	26,300
Kerosene	22,500
Distillate Oils	152,900
Gasoline Transfers	
Refinery	63,000
Terminals	266,000
Service Station Tanks	373,000
Automobile Tanks	498,000
Other Distillate Transfers	98,000
Subtotal, Marketing	2,366,100
6. Total Industry Emissions	4,217,100

we assumed that, for all solvents, 100 percent of the total usage is eventually emitted to the atmosphere. This assumption, coupled with estimated usage of the major industrial chemicals as solvents, allows an estimate of total emissions. The major end uses of solvents were reviewed, particularly for data on their relative contribution to total emissions and the geographical location or distribution of end use.

2. Total Evaporative Emissions

Industrial solvent consumption has been reviewed by Kirk-Othmer (1969). For 1966, they report a total consumption of approximately 12 billion pounds. Of this 12 billion, 4 billion were used in the coatings industry, 2 billion in dry cleaning, 1 billion in metal cleaning and degreasing, and the remainder in the manufacture of inks, adhesives, aerosols, etc.

To obtain a more recent estimate of total usage and total emissions, data on total production of the major chemicals used as solvents was obtained from the U.S. Tariff Commission (1968) and combined with data on estimated solvent usage obtained from the technical and trade literature. The most useful source of estimated end usage was Chemical Profiles [Oil, Paint and Drug Reporter (1966, 1968)]. Other data were obtained from individual issues of the Oil, Paint and Drug Reporter, Chemical and Engineering News, and Hydrocarbon Processing. These data on national total production and solvent usage were compiled to produce Table III-27. If eventual complete evaporation is assumed, annual organic solvent emissions amount to about 7 x 10^6 tons/yr.

In the Nationwide Survey of Air Pollutant Emissions, 1968 [U.S. Department of Health, Education and Welfare (1970)], estimated total emissions from solvent evaporation sources of 3.1 million tons/yr were derived from extrapolation to a national scale of data gathered in four metropolitan areas: Los Angeles, San Francisco, St. Louis, and Washington, D.C.

Table III-28 gives a comparison of total solvent emissions and per capita emissions for some recent area inventories obtained through our survey of pollution control agencies. The per capita emissions range from a low of 7.5 lb/person year for Denver to a high of 60.4 lb/person year for San Francisco. Since most of the inventories are based on estimates rather than actual usage and sales surveys, the range is probably more a reflection of differences

Table III-27 - Industrial Solvents

Solvent	1968 Production (10^8 lb)	Estimated Solvent Usage (10^8 lb)
Special Naphthas	86.5	86.5
Perchloroethylene	6.4	5.7
Ethanol	21.3	5.3
Trichloroethylene	5.2	4.9
Toluene	49.1	4.8
Acetone	13.6	4.1
Xylene	38.3	3.6
Fluorocarbons	8.2 (1969)	3.5
Methyl Ethyl Ketone	4.5	3.2
1,1,1-trichloroethane	3.0	2.8
Methylene Chloride	3.0	2.8
Methanol	38.2	2.7
Ethylene Dichloride	48.0	2.4
Ethyl Acetate	1.8	1.7
Cyclohexane	20.4	1.6
Methyl Isobutyl Ketone	1.8	1.5
Hexanes	2.3	1.3
Benzene	67.0	1.0
n-Butanol	4.3	0.9
Nitrobenzene	4.0	0.5
Turpentine	2.4	0.4
Isopropyl Acetate	0.4	0.4
Ethyl Ether	1.0	0.4
Monochlorobenzene	5.8	0.3
Isopropanol	20.7	0.2
Diethylene Glycol	0.3	0.1
Methyl Acetate	0.1	0.1
Cresols	1.2	0.05
Phenol	15.1	---
Chloroethane (ethyl chloride)	5.7	---
Carbon Tetrachloride	7.6	---
Pinene	1.2	---
Cyclohexanol	7.2	---
Cyclohexanone	4.8	---
Ethyl Benzene	40.3	---
Isobutyl Alcohol	1.1	---
Chloromethane	1.4	---
n-Butylacetate	0.6	---
Methyl Chloride	3.1	---
Total		142.7

Table III-28 - Recent Inventory Data on Solvent Emissions

Region	Date	Population (thousands)	Total Solvent Emissions Reported, ton/yr	Per Capita Emissions lb/person yr
Bay Area APCD	1969	4,100	123,880	60.4
Los Angeles County	1968	7,060	182,500	51.7
Puget Sound APCD	1969	1,907	21,930	23.0
San Diego Air Basin	1968	1,300	15,330	23.6
Orange County	1968	1,318	15,878	24.1
Ventura County	1968	350	2,482	14.2
Monterey and Santa Cruz Counties	1968	355	4,307	24.3
Denver	1969	515	1,919	7.5
Philadelphia AQCR	1968	5,500	43,909	16.0
Greater Cincinnati	1969	1,600	7,491	9.4
New York City	1966	7,980	99,320	24.8
(MSAR Estimate	----	---	---	70)

in assumptions made and sources included in the estimates rather than actual differences in emissions. For those areas which base their data on actual sales and usage surveys (San Francisco and Los Angeles), per capita emissions are at the high end of the range.

For comparison, the HEW estimate of 3.1 million tons/yr is equivalent to about 31 lb/person year. Our estimate, based on industrial usage estimates and total production figures, is equivalent to about 70 lb/person year and is more nearly in agreement with the values for Los Angeles and San Francisco.

3. End Uses and Emissions

The diversity of end uses for organic solvents requires that any review include consideration of only broad, general groupings or categories of end use. The principal categories usually considered are surface coatings, metal cleaning degreasing, dry cleaning, printing and publishing, rubber and plastics processing, adhesives, solvent extraction and miscellaneous usages such as specialty chemicals, drugs and pharmaceuticals and aerosols. Distribution of solvent usage among these end use categories varies widely, depending on the methodology and scope of estimation and the definition of the individual categories. It is generally agreed that surface coating is by far the largest end use of solvents, ranging from 30 to 60 percent of total usage. Other major users in the approximate order of total consumption are degreasing, rubber and plastics, dry cleaning, and printing.

The most complete and detailed breakdown of regional solvent usage has been made by the Los Angeles County Air Pollution Control District in studies leading to legislative action for the control of solvent emissions (Rule 66). These studies and their results have been reported by Lunche et al (1957) and Chass et al (1960, 1963), and also in technical reports by Los Angeles County APCD personnel. Similar studies by the San Francisco Bay Area APCD have been reported by Wohlers (1965) and others.

a. Surface Coatings

Surface coating operations employ the full spectrum of paints, varnishes, lacquers, stains, and shellacs in a variety of application methods. Compositions of surface coatings and particularly the amounts of solvents and thinners used vary with the end use and type of application method. Volatile organic constituents range from less than 10 percent for high solids content coatings for dip and roller application to over 70 percent for spray applications of lacquers, stains and sealants.

Water-base paints, widely used as both interior and exterior architectural coatings, have volatile organic contents of the order of 2 to 5 percent.

By far the bulk of the emissions from surface coating operations result from the end use application and evaporative drying or curing steps. Emissions from the manufacture of coatings have been estimated by Lunche (1957) to be only 1.2 percent of the total volume of coatings manufactured. These emissions result from open or uncontrolled evaporation losses from milling and cooking of the coating components.

Of the end use categories, surface coating operations use the largest quantities of mixed petroleum solvents, both aromatic and aliphatic, as well as significant amounts of the oxygenated solvents - ketones and alcohols - and esters. According to Lunche (1957), surface coating operations account for about 42 percent of the petroleum (naphtha) type solvents and about 38 percent of the ketones, alcohols, esters, and miscellaneous solvents consumed in the LAAPCD.

Recent data from the Bay Area APCD (1969) show that 58 percent of estimated solvent evaporation emissions in the BAAPCD derive from surface coating operations.

Estimates of solvent comsumption by the coatings industry are given by Kirk-Othmer (1969) for 1966 and, more recently, by Yazujian (1971) for 1970. These sources present somewhat conflicting estimates in their breakdown of usage by solvent classes and in their total consumption estimates, as shown in Table III-29.

Table III-29 - Reported Estimates of Solvent Consumption by Coatings Industry

Solvent	Consumption (10^6 lb) Kirk-Othmer (for 1966)	Consumption (10^6 lb) Yazujian (for 1970)
Hydrocarbon		
Aliphatic	1500	600
Aromatic	1000	690
Other	85	---
Total	2585	1290
Alcohols	400	555
Esters	270	250
Ketones	580	815
Miscellaneous	100	275
Grand Total	3935	3185

Although not specifically stated in either of the above references, it is believed that in both cases the estimates are based on data for sales by the manufacturer. Thus, we believe the totals are considerably low because they do not account for solvents and thinners (primarily hydrocarbons) added by the user before appliction.

For industrial applications, and some architectural coatings, dilution or thinning before usage greatly increases the solvent content in the applied coating and thus greatly increases emissions. For example, a typical primer coat for spray coating of appliances with an as-purchased solvent content of 42 percent by weight is reduced about 4:1 with an aliphatic thinner (Kirk-Othmer, 1969). Although this may be an extreme case, estimates of solvent emissions based on as-purchased formulations can be considerably low.

Our own estimate of total solvent usage in surface coatings applications is about twice that given by Kirk-Othmer and Yazujian, or in the range from about 6 to 8 billion pounds per year. This amounts to from about 40 to 55 percent of the total estimated solvent consumption or emissions by all sources, putting our estimate in the range of surface coating emissions estimated from Los Angeles and Bay Area survey data.

b. Degreasing

Degreasing and metal cleaning operations consume large quantities of solvents in operations which range from small parts cleaning in garages and small job shop operations to large production line operations in automobile and aircraft assembly plants. These degreasing operations employ both liquid immersion and vapor phase treatment, or combinations, but, predominantly, the large volume production operations employ vapor phase degreasing.

Losses from degreasing result from vapor loss through the loading ports and tank openings, and from dragout. Kearney (1960) reports solvent makeup of 2.4 gal/hr for a vapor degreasing operation cleaning 40,000 lb/hr of automotive parts. Solvent evaporation has been estimated at 1/2 gallon per day per square foot of tank top opening [Aerospace Industries Association (1968)] for typical vapor degreasers.

Along with dry cleaning, degreasing consumes large amounts of the halogenated solvents. Until the advent of recent restrictions because of its photochemical reactivity, trichloroethylene was the principal solvent used in vapor degreasing. For those users in areas limiting the emissions of trichloroethylene, inhibited 1,1,1-trichloroethane has been satisfactorily substituted with only slight modifications of operating conditions. Other solvents used for specific cleaning operations are perchloroethylene, trichlorotrifluoroethane, and other mixed chloro- and fluorocarbon solvents.

In addition to the halogenated solvents used in vapor degreasing, the numerous smaller operations which rely on immersion cleaning use a variety of available solvents, both halogenated and petroleum solvents. Thus, degreasing emission estimates based on consumption of the major halogenated solvents alone could lead to indeterminately low estimates.

The best estimates of total solvent emissions from degreasing operations are derived from survey data derived from the detailed inventory studies made by the Los Angeles and Bay Area Air Pollution Control Districts. These data indicate that solvent emissions from degreasing range from about 9 to 13 percent of total organic solvent emissions. Thus, we estimated total emissions from this end use category to be in the range from 1.3 to 1.9 billion pounds per year.

c. Dry Cleaning

The dry cleaning of wearing apparel and other textiles consumes significant amounts of both petroleum naphtha and chlorinated hydrocarbon solvents. Principal solvent types are Stoddard solvent (aliphatic, boiling range 310° to 390°F), 140° safety solvent (aliphatic, boiling range 350° to 400°F), and perchloroethylene.

In the 1963 Census of Business, dry cleaning plants using synthetic solvents (principally perchloroethylene) outnumbered those using petroleum solvent and accounted for about 51 percent of total sales receipts. Recent data from the National Institute of Dry Cleaning, reported by McGraw and Duprey (1971), indicate that 50 percent of the plants use petroleum solvents and 50 percent use synthetic solvents. Of the plants using synthetic solvents, 25 percent are reported to be controlled, generally by adsorbent vapor recovery systems.

Emissions from dry cleaning operations occur principally as a result of the drying operation, with lesser amounts being evaporated from still and filter residues disposed of as solid waste. McGraw and Duprey (1971) reported estimated emission factors of 305 lb/ton of clothes cleaned in plants using petroleum solvents and from 35 to 210 lb/ton of clothes cleaned in plants using synthetic solvents, depending on extent of control. These authors reported survey data from California and Michigan which indicated that about 18 lb/person year of clothes are cleaned in moderate climates nd about 25 lb/person year in colder climates. On this basis and the 50/50 distribution of clothes cleaned by petroleum and synthetic solvents, total dry cleaning emissions range from about 300 million to over 500 million pounds per year.

From data reported by the National Institute of Dry Cleaning (1971), total solvent losses from plants using petroleum solvents amount to nearly 500 lb/ton of clothes cleaned in a plant employing a washer-extractor operation with a regenerative filter. Of the nearly 500 lb/ton loss, 76 percent was evaporated to the atmosphere at the plant and 24 percent discarded as residue in the disposal of solids. Based on this higher emission factor of 500 lb/ton of clothes cleaned in plants using petroleum solvents and the data of McGraw and Duprey for the pounds of clothes cleaned per person year, total petroleum solvent emissions are estimated at about 500 million lb/yr.

Regional survey estimates of dry cleaning emissions vary widely, but recent Bay Area data (1969) indicate that dry cleaning operations emit 6.5 percent of the total organic solvent emissions. This is equivalent to 22.2 tons/day for the Bay Area, or about 3.9 lb/person year. Since sources in the Bay Area may be assumed to be better controlled than the average, dry cleaning emissions in other urban areas may be assumed to exceed 4 lb/person year. Extrapolation based on this factor yields a national estimate of about 800 million lb/yr.

For this study, we estimate dry cleaning solvent emissions to be in the range from about 500 to 800 million pounds per year.

d. Printing and Publishing

The graphic arts industry consumes significant quantities of solvents in inks and diluents and for solvent cleaning operations. Emissions relating to this industry are similar to those for surface coatings in that losses occur predominantly at the point of application and end usage, rather than in the manufacture of component materials.

A general review of the air pollution control problems and practices of the graphic arts industry, as well as industry survey data on ink and solvent consumption, has been presented by the Graphic Arts Technical Foundation, Gadomski (1970). Recent reviews of inks and solvents have been presented by Renson (1968), Salomon and Petrone (1969), and Ianetti (1969).

The types and amounts of solvents emitted from printing processes vary widely, depending on the printing process being used. Probably most significant from a total emission standpoint are the gravure processes, rotogravure and flexogravure, since they utilize the so-called solvent type inks, which are highly volatile and fast drying. Newsprint, letterpress,and lithographic inks are the so-called oil type inks which are generally low in volatile solvents content. However, processes using oil type inks which require heat setting or drying at temperatures of 400°F or greater can result in emissions of partially oxidized species. These emissions from high temperature drying, although a small part of total emissions, are often much more noxious and photochemically reactive than emissions from lower temperature evaporation processes.

A current industry trend toward usage of water based inks and solventless formulations may effect significant reductions of solvent emission. However, these developments have not progressed sufficiently to allow any estimate of their total effect.

The solvents used for flexographic and gravure inks listed by Salomon and Petrone (1969) are made up of eight groups: aromatic hydrocarbons, aliphatic hydrocarbons, mixed aromatic and aliphatic hydrocarbons, alcohols, glycol ethers, esters, ketones, and miscellaneous. Boiling ranges vary from below 150°F to about 400°F, but the majority have intermediate ranges of 200° to 350°F.

Letterpress and lithographic ink solvents listed by Ianetti (1969) are either aliphatic hydrocarbons or glycols, with boiling ranges generally ranging from 400°F to over 600°F.

Total solvent usage in ink manufacture was estimated by Renson (1968) at about 170 million pounds for a total ink production of about 850 million pounds in 1967. Of this total solvent in manufactured ink, about 65 percent was used in flexographic and gravure inks.

In addition to the solvents used in the manufactured inks, significant additional solvent is used to dilute the purchased ink before application and for various cleaning operations. From data presented in the Graphic Arts Technical Foundation Report (1970), the total solvent usage in gravure processes is about twice the amount present in the purchased ink. Lunche (1957) gave a breakdown of gravure solvent usage that indicated total solvent usage to be about four times the amount of solvent in inks purchased.

By applying these dilution factors to the estimate of 110 million pounds of solvent in gravure inks (Renson, 1968), total solvent emissions from gravure printing alone would range from 220 to 440 million pounds per year.

Recent community inventories have not estimated printing plant emissions as a separate category. Wohlers (1957) presented a data summary which indicated that about 3.2 percent of total organic solvent emissions in the Bay Area resulted from printing operations. Lunche (1957) gave data for Los Angeles that indicated rotogravure plants emitted about 2.5 percent of total solvent emissions.

Based on these latter inventory estimates, total solvent emissions from printing operations range from about 350 to 450 million pounds per year. We selected this range to represent our best current estimate.

e. Rubber and Plastics

The only estimates of total solvent usage in the manufacture and processing of rubber and plastics are those derived from the area surveys of Los Angeles and San Francisco. Wohlers (1965) estimated total solvent emissions for rubber and plastics processing at 24 tons/day or 8.6 percent of total solvent emissions. Lunche (1957) attributes 10.9 percent of total solvent purchases to the rubber, plastics and adhesives manufacturing industry.

Based on these estimates by Lunche and Wohlers, total nationwide solvent emissions from the manufacture and processing of rubber and plastics may range from 1.2 to 1.5 billion pounds per year.

f. End Use Summary

Estimated total consumption of solvents and, therefore, emissions are summarized on the basis of major end use category in Table III-30.

Table III-30 - Estimated Solvent Emissions by End Use Category

Identified Source	Solvent Emissions (10^8 lb/yr)
Surface Coatings	60-80
Degreasing	13-19
Dry Cleaning	5-8
Printing and Publishing	3.5-4.5
Rubber and Plastics	12-15
Subtotal, Identified Sources	93.5-126.5
Unidentified Sources	16.2-49.2
Total	142.7

F. CHEMICAL PROCESS INDUSTRY

1. General

The chemical process industry, as broadly defined by the Standard Industrial Classification Manual, Bureau of the Budget (1957), encompasses the spectrum of industries lumped under the major product group designation of "chemical and allied products," as SIC 28. The diversity of the chemical industry is illustrated by the membership list of the Manufacturing Chemists' Association, the major industry association representing the chemical industry. Member companies include major petroleum refineries, non-ferrous metal producers, pharmaceutical manufacturers, and rubber and plastics manufacturers, as well as those companies engaged in the manufacture of the commonly considered industrial chemicals.

In the development of criteria for defining and limiting the scope of the present study, a candidate listing of organic chemicals produced in excess of 100 million pounds per year was prepared. A review of the literature was made for information relating to organic emissions from the manufacture or processing of the chemicals in the candidate listing. The trade and technical journals provided essentially no quantitative data on organic emissions from chemical processing, although a great many articles discussed in qualitative terms the successful application of pollution control systems.

2. Industry Emissions

Chemical process industry emissions may be estimated by applying generalized loss factors developed by analogy from the emission factors reported for the petroleum industry. Mencher (1967) used this methodology in treating a typical petrochemical plant producing ethylene from petroleum feed stocks. For the various process equipment and storage tanks in a plant producing 500 million lb/yr ethylene, Mencher estimated emissions by using emission factors developed in the Los Angeles studies of petroleum refining (PHS Publication No. 763, 1960) adjusted for changes in volatility and storage capacity. Using factors for a well-controlled plant operation, Mencher arrived at a figure for total organic vapor loss of 10,430 lb/day or 0.21 percent loss by weight based on feed throughput.

Since statistical data are generally reported in terms of amount of product, Mencher's total loss factor was transformed from a feed throughput basis to a product basis. Since the ethylene yield is about 30 percent of the feedstock, losses from ethylene manufacture are estimated at about 0.7 percent of ethylene produced.

Mencher suggests that similar treatment of other hydrocarbon processing plants would result in estimated emissions ranging from 0.1 to 0.6 percent by weight of feed throughput or about 0.3 to 2.0 percent based on product, assuming a feed-to-product ratio similar to that for the ethylene plant.

Using these generalized loss factors, we made some estimates of total emissions for the entire petrochemical industry. According to Bland (1970), the total aliphatic plus aromatic petrochemical output was 98.3 billion pounds in 1968 and about 113.5 billion pounds in 1969. As shown in Table III-31, the total estimated emissions for this major segment of the chemical industry range from about 2 x 10^5 to about 1 x 10^6 tons/yr.

Table III-31 - Estimated Hydrocarbon Emissions From Petrochemical Production

	Estimated Emissions	
Total Production	Lower Limit[a]	Upper Limit[b]
98.3 x 10^9 lb (1968)	1.5 x 10^5 ton/yr	9.8 x 10^5 ton/yr
113.5 x 10^9 lb (1969)	1.7 x 10^5 ton/yr	1.1 x 10^6 ton/yr

a) Based on 0.3% of production
b) Based on 2.0% of production

The chemical industry's own assessment of its pollution problems, emissions, and extent of control was given in the report of the 1967 survey of MCA member companies (MCA, 1967). This report summarized data obtained from a survey response from 992 chemical plants, representing 396,748 employees in 641 communities nationwide. As shown in Table III-32, the state-by-state breakdown of organic vapor emissions totals 2.88 million lb/day, under existing controls. The estimated emissions would have been about 7 million lb/day without controls.

Table III-32 - Chemical Industry Organic Emissions (pounds per day)

	Organic Particulates (solid or liquid)	Other Organics (gas or vapor)	Estimated Emissions if no Treatment or Control Measures Were in Use Organics
Alabama	3,000	46,000	118,000
Arizona, Nevada, New Mexico, Oklahoma, Utah	†	†	†
Arkansas	†	3,000	3,000
California	13,000	84,000	549,000
Colorado	†	2,000	35,000
Connecticut	5,000	18,000	33,000
Delaware	1,000	4,000	17,000
Florida	1,000	7,000	14,000
Georgia	1,000	1,000	4,000
Idaho, Minnesota, Montana, Nebraska North Dakota, South Dakota, Wyoming	4,000	†	27,000
Illinois	4,000	24,000	68,000
Indiana	7,000	13,000	271,000
Iowa	†	26,000	36,000
Kansas	†	8,000	11,000
Kentucky	3,000	156,000	525,000
Louisiana	13,000	666,000	1,072,000
Maine, New Hampshire, Rhode Island, Vermont	†	†	4,000
Maryland	†	2,000	10,000
Massachusetts	2,000	25,000	54,000
Michigan	11,000	64,000	104,000
Mississippi	†	9,000	14,000
Missouri	†	44,000	115,000
New Jersey	6,000	102,000	441,000
New York	5,000	48,000	87,000
North Carolina, South Carolina	2,000	16,000	42,000
Ohio	15,000	115,000	297,000
Oregon	†	4,000	12,000
Pennsylvania	7,000	79,000	231,000
Tennessee	2,000	149,000	390,000

Table III-32 (continued)

Texas	6,000	925,000	1,814,000
Virginia	1,000	7,000	10,000
Washington	†	†	1,000
West Virginia	35,000	215,000	522,000
Wisconsin	†	19,000	33,000
Total	150,000	2,883,000	7,014,000

†Less than 500 lb/day
Individual quantities rounded to nearest 1,000 lb
Sum of column entires may not exactly correspond to
total on account of rounding

*from MCA (1967)

For our estimate of organic emissions from the chemical industry, the MCA as-controlled value of 2.88 million lb/day was converted to an emission factor based on employment of the plants surveyed, or 7.3 lb/employee day. Application of this factor to the total chemical industry employment of about 1 million (Handbook of Labor Statistics, 1970) resulted in total estimated emissions from this source category of about 1.4 million ton/yr.

This extrapolation assumes no net reduction of emissions due to increased control activity since the 1967 survey. This may be rationalized by assuming that the 1967 survey data were heavily weighted by data from the larger, well-controlled plants and that extrapolation to include all plants offsets any changes due to increased control activity.

G. OTHER INDUSTRIAL PROCESSES

Included in this section are several reviews of industrial processes that do not logically fit into the previous major source categories or for which there is sufficient information to warrant detailed discussion.

1. Carbon Black Manufacture

The carbon black industry has been recently reviewed by the TI-2 Chemical Committee of the Air Pollution Control Association (Drogin [1968]). This review described current industry practices and discusses effluent emissions.

Bureau of Mines (1969) figures for carbon black production in 1968 show that the furnace process, by far, dominates the industry. Of the total 1968 production of 2.81 billion pounds, nearly 2.4 billion pounds were produced by the furnace process. The remaining production is from the thermal black process and, to a lesser extent, the channel process. Because particulate emissions from the channel black process are not controllable, this process is slowly being phased out of existence.

Drogin (1968) presents typical process flowrates and effluent gas compositions for various grades of oil furnace blacks. These are given in Tables III-33 and III-34. The only other effluent gas analyses found in the literature were for a typical furnace process in Great Britain (Allan, 1955) and for a U.S. oil furnace plant of 25 x 10^6

Table III-33 - Typical Oil, Air and Gas Rates Used in Manufacture of Oil Furnace Blacks[a]

Grade Black	Air ft^3/hr	Oil gal/hr	Gas ft^3/hr
Super abrasion	240,000	240	15,500
Intermediate super abrasion	190,000	220	12,200
High abrasion	160,000	210	10,000
Fast extrusion	300,000	750	2,000

(a) From Drogin (1968)

Table III-34 - Typical Composition of Oil Furnace Carbon Black Exhaust Gas[a]

	Composition (vol%, dry basis)	
Component	Large Particle Size Black	Small Particle Size Black
Carbon dioxide	5	4.3
Carbon monoxide	5	11.8
Hydrogen	17-18	13.9
Methane	∿1	0.76
Acetylene	∿1	0.31
Nitrogen	balance	balance
Hydrogen Sulfide (in ppm)	300-400	300-400
Sulfur (in ppm)	200-400	200-400

(a) From Drogin (1968)

lb/year capacity (Shearon, 1952). These latter data are in general agreement with those given in Table III-34, in that the major organic species are methane and acetylene, with some smaller amounts of other low molecular weight hydrocarbons. Dependent on the grade of black being produced, the concentrations of total hydrocarbons emitted range from one to two percent of the effluent gas (for the furnace process), with the ratio of acetylene to methane ranging from 0.5:1 to about 1:1.

Calculated emission factors derived from these data are in general agreement with the values given by McGraw (1970). For oil furnace black production, total hydrocarbon emissions average 400 lb/ton of product. Thus, the total hydrocarbon emissions from carbon black manufacture are estimated to be 3 x 10^5 tons/yr.

The regional distribution of carbon black production shows the emissions to be highly localized, with 22 of the U.S. total of 29 plants being located in Texas and Louisiana.

2. Coke Manufacture

A major use of coal in the U.S. is for the production of coke to be used primarily in blast furnace steel production and, to a much lesser extent, in foundry operations and as fuel. Over 98 percent of the coke produced in the U.S. is made in by-product ovens, with the remainder coming from beehive oven operations. A breakdown of U.S. production and consumption of oven coke by status is shown in Table III-35. Beehive coke production in 1968 was only 775,000 tons, almost entirely in Pennsylvania (355,000 tons) and Virginia (419,000 tons).

A complete description of modern U.S. coke manufacture at an integrated iron and steel operation is given by Varga (1969). Modern slot ovens may typically hold up to 40 tons of coal per charge, with up to 100 ovens in a battery. Charging, coking and discharging operations are arranged sequentially within a battery, so that although basically a batch operation overall operation may be treated as being continuous. Typical coking periods range from 16 to 20 hours. A typical material balance for oven coke operation is shown in Table III-36.

Table III-35 - Oven Coke Production and Distribution in United States, 1968(a)
(in thousand short tons)

State	Produced	Used by Producer		Commercial Sales			
		Blast Furnace	Other	Blast Furnace	Foundries	Industrial	Residential Heating
Alabama	5,462	3,425	472	501	557	369	9
California, Colorado, Utah	3,174	2,941	14	---	b	b	---
Connecticut, Maryland, New Jersey, New York	7,599	6,421	49	985	415	100	b
Illinois	2,074	2,019	76	---	---	b	b
Indiana	8,144	7,467	13	b	b	b	b
Kentucky, Missouri, Tennessee, Texas	2,000	b	b	b	b	96	b
Michigan	3,684	b	b	b	b	b	b
Minnesota, Wisconsin	844	b	b	b	b	b	b
Ohio	8,428	7,224	137	440	b	184	b
Pennsylvania	18,110	16,747	22	283	b	263	b
West Virginia	3,360	2,999	b	---	---	b	---
Undistributed	---	4,068	193	1,136	1,962	871	65
Totals	62,878	53,312	974	3,345	2,934	1,883	113

(a) Data from U.S. Bureau of Mines (1969)
(b) Included in undistributed

Table III-36 - Typical Material Balance for By-Product Coke Oven Operation* (Basis - one net ton coke produced)

Item	Amount (pounds)
Input	
Coal	2950
Output	
Coke + Breeze	2121
By-product Chemicals	290
Coke-oven gas	534 (15,000 ft^3)

*Taken from Varga (1969)

Products of the coking operation are coke, coke oven gas, normally used to fire the coke ovens, and various by-product chemicals, such as phenol, benzene, toluene, naphthalene, tars, and pitches.

The major emission sources and types of pollutants emitted by U.S. coking operations have been described by Varga (1969) and others (Dancy [1970], Fullerton [1967]), but no quantitative data on emissions have been reported. To obtain quantitative estimates of pollutant emissions from coking operations, data from European and Russian sources have been used (United Nations [1968], [1971], Kirchoff [1962]). Except for minor differences in oven size and firing arrangements, European coking practice is quite analogous to U.S. practice and, thus, emissions should be quite similar.

Kirchoff (1962) reported the following analyses of of the gases released during charging of a 30 m^3 oven (17 tons/charge):

Constituent	% by volume
CO_2	6.6-8.0
CmHn	0.4-0.8
CO	2.0-3.8
CH_4	2.0-5.2
H	4.8-10.8
N	75.2-71.4
O	9-0

In actual practice, emissions during charging often ignite and partially burn so that some reduction in organic emissions to the atmosphere occurs.

The United Nations reports (1968, 1971) give estimates of emissions from plants in Poland, Chechoslovakia, France and the USSR. In Tables III-37 and III-38 the data from Poland and the USSR are presented.

Combining the organic emission quantities given in Table III-37 for the Polish plant gives an organic emission total of 3.7 lb/ton coke, or approximately 5.5 lb/ton coal charged.

Totalling emissions quantities for the USSR plant given in Table III-38 result in a considerably lower value for total emissions of about 0.8 lb/ton coke, or 1.2 lb/ton coal charged.

In the National Emission Standards Study, (U.S. Department of Health, Education and Welfare, 1970) an estimate of the total U.S. organic emission from the coking industry is given as 1.5 million tons/year (without supporting references). For the reported production of 66 million tons of coke, this estimate amounts to about 30 lb/ton coal charged or about 45 lb/ton coke produced.

A third estimate of emissions from coking is given by McGraw. His figure of 4.2 lb/ton of coal charged is based on data from the United Nations (1969). For beehive ovens, McGraw recommends a factor of 8 lb/ton coal. Thus,

Table III-37 - Nature and Extent of Atmospheric Pollution Caused by Coke-Oven Batteries*

Serial Number	Pollutant	Chemical Formula	Discharge in kg/t of charge				
			Charging of Chambers	Coking Cycle	Discharging and Quenching	Firing	Total
1	Coal (coke) dust		0.621	0.059	0.182	0.005	0.867
2	Tar		0.104	0.349	0.010	---	0.463
3	Methane and homologues	C_nH_{2n+2}	0.103	0.676	---	---	0.779
4	Ethylene and homologues	C_nH_{2n}	0.015	0.102	---	---	0.117
5	Acetylene	C_2H_2	0.001	0.006	---	---	0.007
6	Carbon monoxide	CO	0.037	0.252	0.005	0.001	0.295
7	Benzene	C_6H_6	0.015	0.087	---	---	0.162
8	Naphthalene	$C_{10}H_8$	0.005	0.034	0.014	---	0.053
9	Phenol	C_6H_5OH	0.006	0.010	0.079	---	0.095
10	Pyridine	C_5H_5N	0.061	0.006	---	---	0.007
11	Ammonia	NH_3	0.008	0.027	0.057	---	0.092
12	Hydrogen sulphide	SH_2	0.012	0.047	0.038	---	0.097
13	Hydrocyanic acid	HCN	0.001	0.003	0.005	---	0.009
14	Oxides of nitrogen	NO	0.013	0.006	---	---	0.019
15	Sulphur dioxide	SO_2	0.011	0.001	---	2.171	2.183
16	Carbon disulphide	CS_2		0.001	---	---	0.001
17	Chlorine	Cl_2	0.001	0.003	---	---	0.004
18	Chlorides	Cl^-	---	---	0.028	---	0.028
19	Sulphates	SO_4	---	---	0.072	---	0.072
	Totals		0.96	1.45	0.49	2.17	5.29

Table III-38 - Types and Quantities of Air Pollutants in the Vicinity of Coking and By-Product Plants (USSR)*

Source of pollution, or operation accompanied by discharge of noxious substances	Pollutant discharged	Quantity discharged (in tons per day)	Duration of emission for each operation (in minutes)	Number of operations per day	Remarks
1. Coke-oven charging	Coal dust	0.530	4-5		
	Carbon monoxide	0.220	4-5	106	The figures given are for a single battery
	Sulfur dioxide	0.060	4-5		
	Benzene hydrocarbons	0.057	4-5		
	Hydrogen sulphide	0.030	4-5		
2. Discharging	Coke dust[a]	0.300	0.6	106	The figures given are for a single battery
	Carbon monoxide	0.064	0.6		
3. Quenching of coke with waste, water steam-circulated to remove the phenol	Hydrogen sulphide	0.580	2		
	Phenols	0.240	2		The figures given are for a single quenching tower serving two batteries
	Ammonia	0.240	2		
	Sulfur dioxide	0.145	2	212	
	Cyanide compounds	0.001	2		
4. Coke-oven battery waste-gas flues:					
(a) ovens heated with coke-oven gas having hydrogen sulphide content reduced to 3 g/Nm³	Sulfur dioxide	1.830	Continuous		Per flue evacuating one battery's combustion products
(b) ovens heated with blast-furnace gas	Carbon monoxide	21.900			
5. Wagon-tippler	Coal dust	0.045	0.1	175	Unloading wagons of 60 T capacity
6. Chimneys of coal preparation shed drier plant	Coal dust	15.600	Continuous		
	Sulfur dioxide	6.720			For a twelve-drum drier plant
7. Equipment and tanks of coke-oven gas condensation and cooling plant[b]	Ammonia	0.0064			
	Phenols	0.0025			
	Pyridine bases	0.0006			
	Hydrogen sulphide	0.0006			
	Hydrogen cyanide	0.0003			
8. Condenser pump room	Ammonia	0.0081			
	Phenols	0.0037			For a twelve-drum drier plant
	Hydrogen sulphide	0.0032			
	Pyridine bases	0.0005			
	Hydrogen cyanide	0.0004			
9. Engine room	Carbon monoxide	0.0173			
	Benzene hydrocarbons	0.0093			
	Hydrogen sulphide	0.0053			
	Ammonia	0.0022			
	Naphthalene	0.0005			
	Organic sulfur compounds	0.0005			
	Hydrogen cyanide	0.0003			
	Pyridine bases	0.0002			

(a) Dust of relatively large particle size, settling rapidly and therefore not causing protracted pollution of the atmosphere

(b) The discharge from these installations and from those listed subsequently is continuous

* Daily capacity of 10,000 (dry-charge), four battery operation

estimates of total emissions from the various source data may range from a high (USDHEW) of 1.5 x 10^6 ton/year to a low of 2.6 x 10^4 tons/year (USSR).

For our estimate of organic emissions from the coking industry, we used McGraw's emission factors. Thus, our estimate of total emissions from coking is about 2 x 10^5 tons/year.

The specific compounds emitted are most probably those types of organics listed by the UN report (see Tables III-37 and III-38).

The emissions of polynuclear aromatic hydrocarbons, primarily associated with the particulate emissions from coking, are summarized in reports by Hangebrauck (1967) and GCA Technology (1970). GCA Technology reviewed data from several sources and derived an average emission factor for benzo-a-pyrene (BaP) from coking operations of 1.8 grams per ton of coal processed. Estimated total BaP emissions are thus about 180 tons/year.

A recent analytical study of polynuclear aromatic hydrocarbon emissions from coke production is reported by Searl (1970). Searl summarizes the data from analysis of effluent samples taken from twenty different coke oven plants and gives ranges of composition of eight specifically identified polynuclear aromatics.

3. Wood Pulping Industry

Emissions from the wood pulping industry have been studied by Environmental Engineering, Incorporated (1970). However, no mention is made of non-sulfur containing organic emissions. In a further review of the literature, only two publications relate any information on such emissions.

Walther and Amberg (1970) describe an advanced control system in operation at a 500 ton per day Kraft mill at Fairhaven, California and give the following values for non-sulfur emissions from the major source points (after control):

Source	Acetone (lb/day)	Methanol (lb/day)	α-Pinene (lb/day)	Unidentified Non-Sulfur Organics (lb/day)
Washer seal vent tank	11	146	715	
Washer hood vent	25	92	116	
Knotter hood vent	14	95	20	500
Black liquor oxidation	85	708	91	
Digester*	50	27	118	—
Totals	185	1068	1060	500

*Without incineration of digester non-condensibles

Comparison of the flow sheet for the Fairhaven plant with the Kraft process flow sheets given in the EEI report indicates that the Fairhaven plant may well be the only in the U.S. using such advanced control technology. However, the emissions tabulated by Walther and Amberg were used in this study to obtain a crude estimate of the total emissions from Kraft pulping, since a brief search of the literature revealed no other tabulation of non-sulfur containing emissions.

Because the Fairhaven plant uses softwood only, the estimate of emissions is based only on the softwood Kraft tonnage, which for 1968 was 18,440,000 tons or about 76 percent of the total Kraft tonnage. Assuming the average emissions to be those of the Fairhaven plant with no digester off-gas incineration, total U.S. emissions (1968 levels) are estimated as shown in Table III-39.

Thus, even though the estimates shown in Table III-39 are uncertain because of the assumptions made and data are lacking on other pulping processes, it can be seen that the pulping industry is a significant source of non-sulfur containing organic emissions.

Table III-39 - Estimated Non-Sulfur Organic Emissions from Wood Pulping

Pulping Method	Pulp Production (10^6 ton)	Organic Emissions (10^3 tons/yr)				
		Methanol	Acetone	α-Pinene	Unidentified	Total
Kraft, soft wood	18.4	20	3.4	20	9	52.4
Kraft, hard wood	5.9	no data				
Sulfite	2.5	no data				
NSSC	3.5	no data				
Dissolving	1.5	no data				
Soda	0.2	no data				

According to Kirk-Othmer (1969), total 1968 U.S. production of all grades of turpentine from wood pulp processing was 32.9 million gallons. Approximately 15 percent of this total was used for solvent purposes, equivalent to about 17,600 tons. Thus, estimated emissions of α-pinene from Kraft mills more than equals the total used for solvent purposes.

The only other article found relating to potential non-sulfur organic emissions was by Miller (1968). In his study of improved methods of turpentine recovery, Miller estimated the total amount of turpentine lost to the atmosphere as a result of incomplete recovery as 15 million gallons annually. This amounts to about 54 thousand tons, or about 2-1/2 times the estimate of total industry emissions of α-pinene based on Walther and Amberg data.

According to Miller, industry recovery of turpentine currently averages 60 to 70 percent of the potentially available turpentine. Thus, the 15 million gallons lost would be in reasonable agreement with the 32.9 million gallons total production cited by Kirk-Othmer.

4. Phthalic Anhydride Manufacture

A specific study of air pollution from phthalic anhydride manufacture was reported by Fawcett (1970). This report reviewed the process chemistry, potential emissions, and control technology.

The ranges of concentration for the major pollutants in the effluent from a dry recovery (product condenser) process prior to abatement are as follows:

Contaminant	Concentration (ppm)
phthalic anhydride	40-200
maleic anhydride	100-600
naphthoquinone	10-30
benzoic acid	5-40
aldehydes (as CH_2O)	10-100

Total organics emissions thus range from 300 to 1200 lb/hr for a 100 million pound per year plant, depending on type of process, condenser operation, etc.

The two major control methods, wet scrubbing and incineration, were described by Fawcett, with newer plants tending to choose incineration as the preferred method. However, no estimate of the extent of existing industry control is given.

Based on the above emissions and the 1968 production of 744 million pounds, total organic emissions, without controls, could range from 10,000 to 40,000 tons per year. Since the total production is manufactured at only sixteen locations in the U.S., the pollution load at a specific location could cause a significant localized problem. Of the sixteen plant locations, there are four each in New Jersey and Illinois, three in Pennsylvania, two in California and one each in Texas, Ohio, and West Virginia.

5. Synthetic Rubber and Plastics

A limited amount of information on emissions from synthetic rubber and plastics processing is reported from plant studies made as part of the Louisville Air Pollution Study (Public Health Service, 1961). For one plant engaged in production of synthetic rubber (butadiene-styrene and butadiene-acrylonitrile copolymers) and polyvinyl chloride resins, air contaminant analysis and material balances result in estimates of emissions from major processing areas. Principal emissions are the monomers emitted during polymerization and milling.

For PVC resin manufacture, conversion of plant data to an emission factor basis results in an estimate of 17 lb of vinyl chloride per ton of plastic processed, from all processing steps.

For synthetic rubber manufacture, similar treatment results in emission factors for butadiene and acrylonitrile of 40 and 17 lb/ton of rubber processed, respectively.

Applying these estimated emission factors to total reported quantities manufactured gives crude estimates of total emissions. For PVC resins and plastics, the 1968 production of PVC and copolymers was 2.6 billion pounds, or 1.3 million tons. Total vinyl chloride emissions thus could approximate 22 million pounds, or 11 thousand tons.

The 1968 production of butadiene elastomers was 2.5 billion pounds for butadiene-styrene type and nearly 0.3 billion pounds of butadiene-acrylonitrile type. Application of the emission factors to these total amounts results in estimated emissions of about 26 thousand tons of butadiene and nearly 2 thousand tons of acrylonitrile.

H. GEOGRAPHICAL DISTRIBUTION

1. Introduction

The estimation of organic air pollutant emissions and ranking of sources on a nationwide basis presents only a partial view of the total problem. Of significant importance are the regional geographic and demographic distributions of the sources, emissions and adverse effects. Since the primary impetus of air pollution control is a concern for the welfare of the human population, efforts have been made to analyze those factors which illustrate the relative distribution of pollutants and people.

2. Source Distribution

In previous discussions of major emission sources, nationwide estimates of sources and emissions are broken out, where possible, to show distribution at a state level, as well as pointing out regional concentrations of certain industrial sources. In this section, further discussion of the geographic distribution and ranking of sources and emission is considered. Several possible arrangements or groupings of the major emission source categories may be treated in developing geographical ranking. For example, each of the source categories could be handled independently and then combined in various ways to show overall distribution by regions, states, Air Quality Control Regions (AQCR's), or Standard Metropolitan Statistical Areas (SMSA's).

A somewhat different, and perhaps more logical method of arrangement is to initially treat the sources as two separate groups. The first group is made up of those sources for which actual geographic location can be specified or which show a strong correlation with general population density. In this first group would fall the major sources exemplified by petroleum refining, chemical process industries, fuel combustion, gasoline storage and marketing, and that portion of the solid waste combustion source that derives from urban waste disposal.

The second group consists of those sources which are so diffuse as to make specified source location impossible or, at best, overly detailed for a study such as this and which show little or no correlation with general population density distribution. This second group is exemplified primarily by the largest single source category, solvent evaporation.

It is to this latter group that we devoted the most attention, since any desired breakdown of those members of the first group is obtained by a relatively straightforward compilation of available statistics.

a. Solvent Emission Sources

Solvent evaporation emissions, except for those attributable to dry cleaning and, perhaps, the trade sales of paint and varnish products, are not directly population dependent. Solvent emissions from dry cleaning, which account for about 5 to 8 x 10^8 lb/year solvent emissions may be distributed on a regional basis according to percentage factors derived from dry cleaning receipts reported in the 1967 Census of Business (Selected Services, BC67-SA1, 1970).

Some information on regional distribution of solvents used in surface coating applications may be obtained from Commerce Department statistics on the regional shipments of paints and allied products from manufacturing establishments. These data, however, do not necessarily reflect consumption patterns and, therefore, ultimate solvent emissions.

Regional distribution of sales of paints and allied products by merchant wholesalers is given in the 1967 Census of Business (BC67-W52, 1970). According to definitions used to characterize paint sales, these data probably represent the so-called "trade sales" products. Trade sales paints include primarily the interior and exterior architectural coatings, although sizable amounts of automotive and machinery finishes and other non-architectural paints are also handled by trade sales wholesalers.

Industrial coatings are sold directly to the manufacturers of machinery and various finished goods and thus distribution of these products may best be represented by the regional distribution of the major manufacturing industries.

The 1967 Census of Business (BC67-WS6, 1970) reports bulk storage capacity and state and county sales figures for the common petroleum products, including special naphthas. Further examination of the sales of special naphtha shows, however, that the reported figures are, in some cases, for very large bulk terminals serving state-wide or even multi-state areas.

For example, total U.S. bulk terminal sales of special naphtha for 1967 was 498.7 million gallons. Of this total, 271 million gallons, or about 45 percent, are represented in sales from ten counties, as shown in Table III-40. Rather obviously, these sales cannot reflect ultimate consumption within that particular county. However, if the reported sales are treated on a statistical region basis, the distribution may better illustrate usage patterns. Thus, the reported state sales have been combined to give regional totals.

Geographical distribution of solvent usage and, therefore, emissions at levels more detailed than the major statistical regions is thus seen to be highly speculative, at least for industrial solvent usage. For this study, distribution of solvent emissions was therefore limited to estimates at a census region level.

The parameters finally used for estimating geographical distribution of solvent emissions were regional sales receipts data for dry cleaning and special naphtha solvents and regional manufacturing employment for all other solvents.

More detailed treatment of solvent emissions by end use category was not believed to be justifiable. For example, distribution of trade sales paints as a separate category would require estimation of solvent content of trade sales paints and also could result in some indeterminate amount of double counting of special naphtha solvents.

b. Total Emission Sources

As was mentioned in previous discussion, the geographical distribution of the majority of emission sources shows a correlation with population distribution or can be estimated from industry statistics. Thus, the development of a rationale for solvent distribution allows estimation of total emissions from each of the major sources on a regional basis.

Table III-40 - Special Naphtha Sales from Bulk Terminals in Ten Highest Counties

County	1967 Sales 10^3 gallons
Middlesex County, New Jersey	97,975
Cook County, Illinois	41,616
Los Angeles County, California	36,453
Baltimore (City), Maryland	22,368
Mecklenburg County, North Carolina	19,645
St. Louis (City), Missouri	12,014
Hamilton County, Ohio	11,868
Kings County, New York	10,273
Harris County, Texas	10,109
Multnomah County, Oregon	8,992
Total	271,313

Table III-41 tabulates the variables used to distribute the emissions of each individual source category among the census regions. The definition of geographical regions used for this distribution is that employed by the Bureau of the Census for census regions.

Application of the distribution parameters shown in Table III-41 to the total hydrocarbon emissions from the major sources and subsources then allows regional distribution of emissions, as shown in Table III-42. The final columns of this table give total hydrocarbon emissions for each region and an emission density factor in tons per square mile/year.

To illustrate the calculations employed in developing Table III-42, the calculation of the dry cleaning solvent emissions for the New England region are described. From the regional dry cleaning sales receipts data, sales receipts for the New England region were $112 million or 5.8 percent of total U.S. receipts. Applying this regional percentage to the total national estimate of emissions from dry cleaning, 4×10^5 tons/yr, then yields annual emissions of 0.2×10^5 tons for the New England region.

Totalling similarly the regional emissions from other source categories results in annual hydrocarbon emissions from all sources in New England of $118. \times 10^5$ tons. By dividing this total emissions estimate by the regional area, 66.6 thousand square miles, yields the estimated total emission density of 17.7 tons/square mile year.

Because of the simplifying assumptions used in this estimation of geographical distribution of total hydrocarbons, some minor inconsistencies occurred. For several major source categories, subdivisions of the major sources were lumped somewhat differently than in the national estimate. The petroleum industry emissions were lumped into four subdivisions: crude oil production; non-refinery crude storage; petroleum refining and all refinery storage of both crude and refined products; and all petroleum product marketing. Also, the miscellaneous industrial process sources were lumped together and distributed according to manufacturing employment, even though such sources as coke production and carbon black manufacture are known to be highly localized.

Table III-41 - Parameters for Regional Distribution of Total Hydrocarbon Emissions

Emission Source Category	Distribution Parameters
Solvent Evaporation	
Dry cleaning solvents	Regional sales receipts
Special naphtha solvents	Wholesale trade sales
All other solvents	Manufacturing employment
Petroleum Industry	
Crude oil production	Crude production statistics
Crude oil storage (non-refinery)	Crude storage statistics
Petroleum refining and refinery storage	Refinery capacity statistics
Product marketing	Gasoline consumption statistics
Solid Waste Combustion	
Municipal and domestic	Total population
Industrial	Manufacturing employment
Agricultural Burning	Agricultural sales statistics
Fuel Combustion	Fuel usage statistics
Chemical Industry	MCA survey statistics
Other Industrial Processes	Manufacturing employment
Forest Wildfires	Forest acreage statistics

Table III-42 - Distribution of Total Hydrocarbon Emissions by Source Category and Census Region (Emission quantities in 10^5 tons/year)

Source Category / Census Region	Dry Cleaning Solvents	Special Naphtha Solvents	All Other Solvents	Crude Oil Production	Crude Oil Storage (non-refinery)	Refinery & Refinery Storage	Petroleum Product Marketing	Municipal & Domestic Waste Combustion	Industrial Waste Combustion	Agricultural Burning	Fuel Combustion	Chemical Industry	Other Industrial Processes	Forest Wildfires	Total Hydrocarbon Emissions	Total Emission Density Tons/sq mi
New England	0.2	2.3	2.0	---	---	---	0.9	1.0	2.2	0.8	0.3	0.2	0.8	1.1	11.8	17.7
Middle Atlantic	0.8	11.5	5.5	---	0.1	1.7	2.6	3.3	6.2	2.2	0.9	1.1	2.3	1.1	39.3	38.3
East North Central	0.8	7.4	6.5	---	0.6	2.7	3.4	3.6	7.3	7.1	0.9	1.1	2.7	1.7	45.8	18.4
West North Central	0.3	2.6	1.5	0.2	0.2	0.9	1.7	1.4	1.7	10.4	0.3	0.4	0.6	1.5	23.7	4.6
South Atlantic	0.7	7.3	3.1	---	0.1	0.3	2.7	2.7	3.5	4.9	0.6	1.2	1.3	3.9	32.3	11.6
East South Central	0.3	2.3	1.3	0.1	0.2	0.5	1.1	1.2	1.5	2.8	0.3	1.8	0.6	2.3	16.3	9.0
West South Central	0.4	2.9	1.3	2.2	2.5	6.6	2.1	1.7	1.5	4.8	0.3	7.7	0.6	2.5	37.1	8.5
Mountain	0.1	0.9	0.4	0.4	0.4	0.6	0.8	0.7	0.4	3.0	0.1	---	0.2	5.1	13.1	1.5
Pacific	0.5	6.1	2.5	0.5	0.7	2.4	2.3	2.3	2.8	5.7	0.3	0.5	1.0	7.7	35.3	3.9
Total U.S.	4.0	43.3	24.1	3.4	4.7	15.7	17.6	18.0	27.0	42.0	4.0	14.0	10.0	27.0	254.7	7.0

Of some interest for control planning purposes are the regional distributions of total emissions relative to total population. Figure III-2 shows in bar graph form the percentage of total U.S. hydrocarbon emissions and the percentage of total U.S. population for each of the regional areas.

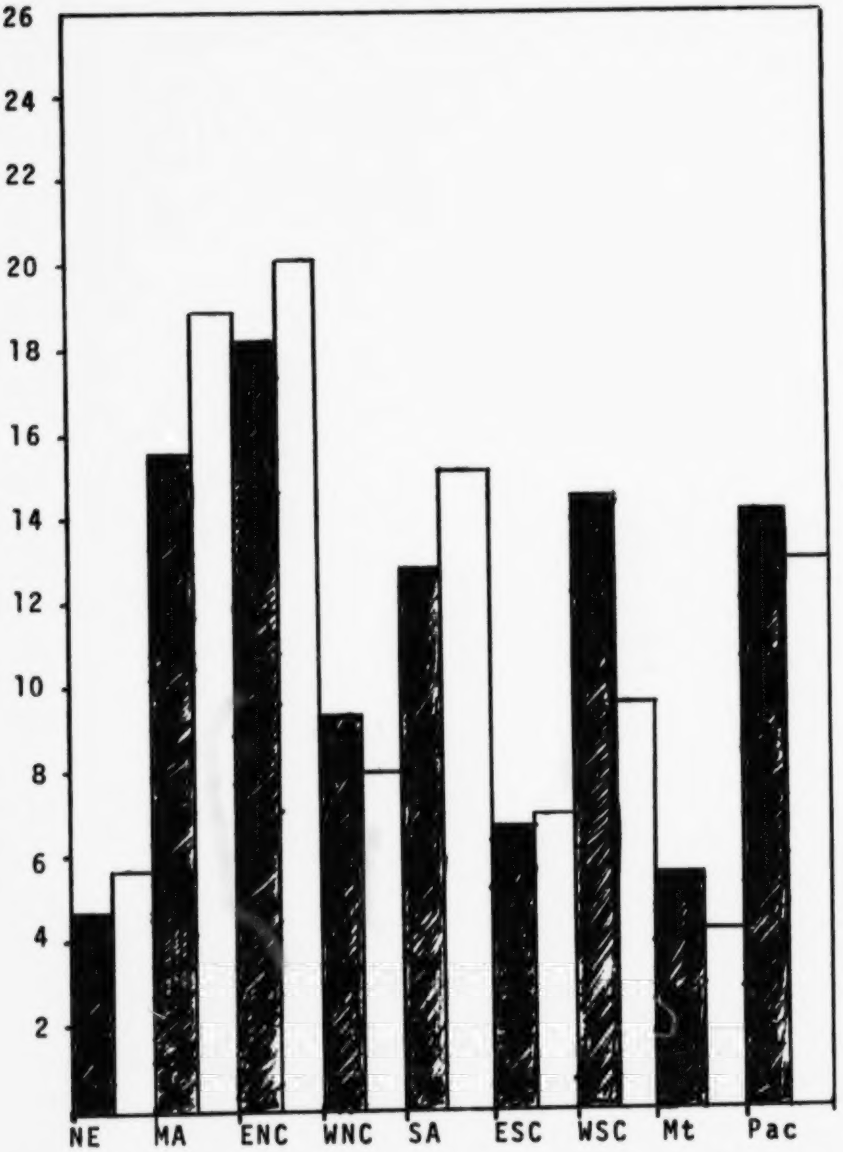

Figure III-2 - Percentage Distribution of Emissions and Population by Census Region

CHAPTER III

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IV. ADVERSE EFFECTS OF HYDROCARBON POLLUTANTS

A. INTRODUCTION

An analysis of the total picture of atmospheric pollution by hydrocarbons requires consideration of the adverse effects on human health and welfare. As a basis for ranking of pollutants and sources establishing priorties for future R&D,reviews of the literature were conducted to assess the adverse effects of hydrocarbon emissions.

It is generally accepted that human health is the predominant concern in efforts to control air pollution. As an example, under the Clean Air Act as amended, human health was the only factor taken into account in setting primary standards for ambient air quality. In this study, however, attempts to define in quantitative terms the health effects related to hydrocarbon air pollutants could not be supported by data in the literature. Definition and quantification of human health effects were precluded by lack of field or laboratory studies under conditions of chronic exposure to low concentrations of hydrocarbons and by complicating effects of atmospheric reactions of hydrocarbons and their synergism with other atmospheric contaminants.

The Air Quality Criteria for Hydrocarbons (U. S. Department of Health, Education and Welfare, 1970) incorporated a review of the current state of knowledge relating to adverse effects of hydrocarbons. The conclusions based on that review were that hydrocarbons, per se, do not present a significant health hazard in ambient air but should be controlled or restricted on the basis of their contribution to photochemical smog and the resultant adverse effects of the smog products.

Literature data relating to the adverse effects of hydrocarbon pollutants are reviewed in the following sections, with particular emphasis on references that would provide quantitative or semi-quantitative input for ranking the pollutants and sources identified in Chapter III.

B. HEALTH EFFECTS

1. Introduction

In any review of air pollutants, a consideration of human health effects is of prime importance. This section presents an evaluation of the available information, published and unpublished, on the contribution of hydrocarbon emissions from stationary sources to adverse effects on human health.

2. Organic Solvents

A major contributor of hydrocarbon contamination from stationary sources is organic solvent evaporation. Sources of these emissions include the manufacture of rubber and plastic products, dry cleaning operations, chemical manufacturing, printing and the manufacture and application of protective coatings. Sixteen of the industrially important solvents are considered here (Table IV-1).

Solvents that exhibit essentially no buildup in the body under conditions of occupational exposure, i.e., 8 hours per day, 5 days per week, are listed below (Patty, 1962, Fairhall, 1969).

Methyl ethyl ketone
Methyl isobutyl ketone
Ethyl acetate
Acetone
Methylene chloride
Methyl chloroform (1,1,1-trichloroethane)
Hexanes
Isopropyl alcohol
Ethyl alcohol

Of the remaining solvents in Table IV-1, toluene and the xylenes are reported to undergo only slight buildup in the human body at moderate levels of occupational exposure.

Chronic occupational exposure to 100 ppm toluene produced no distinct symptoms or after effects. Although some of the absorbed toluene is exhaled, the major portion is oxidized to benzoic acid, conjugated with glycine, and excreted as hippuric acid.

Although xylenes appear to have greater toxicity than toluene, these substances tend to react similarly in the body and are predominantly metabolized and/or excreted.

Methanol and n-butanol exhibit some buildup potential; however, after occupational exposures of 100 ppm for 10 years, no systemic effects were observed.

Table IV-1 - Industrially Important Solvents

Solvent	TLV(A) (ppm)	STL(B) (ppm/min)	LD_{50}(C) (mg/kg-rats)	Smog Chamber(D) Eye Response	Vapor Irritant(E)	Chemical Poison(F)
Petroleum Naphtha	Var.	500/30		119 (II)	0	1
*Isopropanol	400	400/30	5,840	318 (I)	1	2
Perchlorethylene	100	200/30			1	2
*Ethanol	1000	5000/15	13,600		1	1
Trichlorethylene	100	200/30			1	2
Toluene	200	600/30		106 (II)	1	2
*Acetone	1000	1000/30	10,700	303 (I)	1	0
Xylenes	100	300/30		111 (II)	1	2
*Methyl Ethyl Ketone	200	300/5	6,860	295 (I)	1	2
*1,1,1-Trichloroethane	350	1500/5	12,300		1	2
*Methylene Chloride	500	1000/30			2	2
Methanol	200		15,800		1	2
*Ethyl Acetate	400	1000/15	5,000		1	2
*Methyl 1-Butyl Ketone	100	400/5	2,080	213 (I)	1	1
*Hexanes	300-500	500/30			0	1
n-Butanol	100	150/30	4,360		1	2

A through F, see Notes on Table IV-1

*Compounds listed previously that exhibit no buildup in the body.

NOTES ON TABLE IV-1

A. TLV (in parts per million) = Threshold Limits Values published by American Conference of Governmental Industrial Hygienists. They refer to airborne con-concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect.

B. STL (Short Term Limits for Exposure to Airborne Contaminants - A documentation - Pennsylvania Department of Health, Division of Occupational Health). 500/30 = 500 parts per million for 30 minutes.

C. LD_{50} - The dosage which when applied to rats in a single oral dose caused mortality in 50% of the exposed animals.

D. Smog Chamber Eye Response - Expressed in arithmetic mean seconds of exposure time to produce positive feelings of irritation - a very subjective measurement. (Bracketed numbers are relative ranking numbers, with I expressing low reactivity, II intermediate reactivity, and III high reactivity.)

E. Vapor Irritant - Based on the likelihood of developing injury and on the severity and permanence of that injury.

0 = chemicals that are non-volatile or the vapors from which are non-irritating to the eyes and throat.
1 = chemicals that cause a slight smarting of the eyes or respiratory systems (temporary) if present in high concentrations.
2 = chemicals that cause moderate irritation (temporary) such that personnel will find high concentrations unpleasant.

F. Chemical Poison - Rates the hazard from chemicals that enter the body through inhalation, oral ingestion, or skin penetration to cause bodily harm.

0 = no likelihood of producing injury.
1 = minimum hazard. Includes most chemicals having TLV above 500 ppm.
2 = some hazard, typically having TLV of 100 to 500 ppm.

Trichloroethylene is retained in the body for some period after exposure, as shown by analysis of expired air hours to days later. Experimentally, however, no demonstrable intoxication or behavioral effect was evident in rats exposed to 200 ppm for 7 hours per day, 5 days per week, for a 6-month period.

Perchloroethylene has been identified as an irritating lachrymator with narcotic effects above 200 ppm but moderate exposures are not expected to cause any permanent injury. No pathological effects were observed in rats exposed to 70 ppm for 8 hours per day, 5 days per week for 7 months.

Because petroleum naphtha is not a single compound as are most of the other industrially important solvents, it varies in composition and generalizations are therefore difficult. Although a significant portion of the mixture may be aromatic in nature, these components are usually shown to be substituted aromatics such as toluene, xylenes, etc. The classical studies of Gerarde (1962, 1963) show that changes in chemical composition decrease the chronic toxicity potential so markedly that no serious chronic health effects of the type produced by benzene need be expected from inhalation exposure to petroleum naphthas (Deichmann, 1969).

Table IV-1 summarizes available data regarding industrial solvents, including data on Threshold Limit Values (TLV), short-term limits for exposure (STL), chemical poison effects (National Academy of Sciences, 1970), smog chamber eye irritation response (Levy and Miller, 1970), and LD_{50}* (Fairhall, 1969; Deichmann, 1969; Patty, 1962; Sunshine, 1969). Because of variations of conditions and considerations upon which these data are based, this table can serve only as a useful guide rather than as an authoritative ranking of the health effects of the materials listed.

3. Unsaturated Aliphatic Hydrocarbons

Frequent mention of the unsaturated aliphatic hydrocarbons in ambient air warrants a review of their contribution or potential contribution to adverse effects on human health. Analyses of ambient air samples taken during air pollution episodes in 1965 in Riverside, California, identified the following unsaturated hydrocarbons (Stephens, 1967):

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*LD_{50} = Lethal dosage effecting 50 percent mortality in exposed subjects.

Ethylene concentrations ranged from 1.1 to 15.4 parts per billion.
Propylene concentrations ranged from 0.3 to 3.0 parts per billion.
1-Butene concentrations ranged from 0.2 to 0.6 parts per billion.
Isobutene concentrations ranged from 0.3 to 1.0 parts per billion.
1-Pentene concentrations ranged from <0.1 to 0.4 parts per billion.
2-Methyl butene-1 concentrations ranged from 0.2 to 0.8 parts per billion.
Acetylene concentrations ranged from 1.0 to 31.0 parts per billion.
Methyl acetylene concentrations ranged from <0.1 to 1.4 parts per billion.

The low concentrations reported were detected in relatively clear weather, while the high concentrations were detected during an unusually heavy haze. These and other potentially important unsaturated aliphatic hydrocarbons are discussed below.

a. Olefins - Industrially important olefins are ethylene, propylene, and butylenes formed as by-products of the carcking of petroleum fractions and used mainly for polymer synthesis. The lower members of the olefin series (2, 3 and 4 carbon chains) are weak anesthetics or simple asphysiants. As the chain length increases, anesthetic potency increases also.

No threshold limit values (TLV) have been established for these olefins by the American Conference of Governmental Industrial Hygienists (1970 listing). Ethylene, the only olefin listed, is designated a simple asphyxiant. A TLV is not recommended for each simple ashpyxiant because the limiting factor is the available oxygen. Gerarde (1962) has suggested 1000 ppm as the threshold limit value for these olefins.

Effects on the health of workmen exposed to low concentrations of olefins for prolonged periods or to higher concentrations for relatively short periods of time do not appear to warrant serious consideration unless the olefins encountered in sufficient concentrations to cause asphyxia.

While olefins in themselves do not appear to be injurious to human health at concentrations usually found in ambient air, they are instrumental as reactants in the atmosphere in the formation of photochemical smog, via peroxyacyl nitrates (PAN), which are reasonably well established as lachrymators (Christman, 1969).

b. Diolefins - Butadiene and isoprene (2-methyl-1, 3-butadiene) were included as representative diolefins in our review. Experiments on humans and on laboratory animals have demonstrated that 1,3 butadiene has a low order of toxicity and probably has no cumulative effects (API, 1959). The TLV established by ACGIH (1970) is 1000 ppm. In high concentrations, 1,3-butadiene is an anesthetic which can cause respiratory paralysis and even death.

Isoprene appears to be a more potent anesthetic than butadiene, but pharmacologically is similar. No TLV has been established (Gerarde, 1962).

c. Acetylene - No evidence of deleterious effects on health was apparent in repeated exposure to tolerable levels of acetylene. ACGIH (1970) lists acetylene as an inert gas, a simple asphyxiant. On the basis of the lower explosive limit, however, acetylene concentrations should not be permitted to exceed 5000 ppm in the occupational environment.

Methyl acetylene is listed as a simple anesthetic and in high concentrations as an asphyxiant. The recommended TLV is 1000 ppm (Sax, 1963).

d. Gasoline Evaporation - Gasoline is a complex mixture of hydrocarbons, principally paraffins, naphthenes, olefins, and aromatics, as well as dyes, inhibitors and antiknock agents (API Toxicological Review, 1967). Since the composition of gasoline varies greatly depending on blending, seasonal requirements, and intended use, a single TLV for all types of gasoline no longer applies. To determine which TLV is applicable for a particular gasoline, its aromatic hydrocarbon content must be considered (Documentation of TLV, 1971).

Severe reactions, such as depression of the central nervous system, anorexia, vomiting, narcosis and even death, can be produced by inhalation of gasoline vapors at very high concentrations. The most severe cases of gasoline vapor inhalation reported most frequently involved persons entering tanks containing nearly saturated vapor concentrations of gasoline.

Reduced availability of oxygen may also play an important role in effecting asphyxia in tank operations.

In repeated work day exposures to low concentrations of gasoline,effects have been varied and vague. Considering periods of up to 10 and 12 years in some instances, Machle (1941) concluded that no signs of gasoline intoxication were evident in filling station attendants, garage mechanics and tank wagon drivers. Barrel fillers, who are exposed in their work day to concentrations that might be intolerable to many people often complained of anorexia, nausea and nervousness. Eye irritation produced from exposure to low concentrations of gasoline vapors (200 ppm and 500 ppm) was reported by both Davis et al (1960) and Drinker (1943). Gerarde (1962) suggests that no conclusive evidence can be found for harmful effects due to repeated exposure to low levels of gasoline vapors in work atmospheres.

4. Aldehydes

Aldehydes have been reported extensively in the literature as components of photochemical smog, the major effects on humans being reported as irritation of the eyes, respiratory tract and skin. Fassett (1963) indicates that definitive cumulative organic damage to tissues is not commonly found, possibly because the aldehydes are readily metabilized in the body. The irritant effect decreases with increasing molecular weight within a given aldehyde series, and the toxicity generally decreases as the chain length increases.

Most information on aldehyde toxicity is related to the effects of actue exposures. There is a dearth of data pertaining to long-term exposures to low concentrations to aldehydes which would correspond to the conditions of community or ambient air pollution.

Fassett reports (1963) that no discomfort is noted below 2 ppm of formaldehyde during an 8-hour exposure. At concentrations above 2 but below 4 ppm for a similar period, a mild tingling sensation may be noticed in the eyes , nose and pharynx. Concentrations of 10 ppm cause profuse lacrimation and can be endured for only a few minutes. Above 10 ppm, breathing becomes difficult. However, when the subject is removed from such exposure, the symptoms subside; lacrimation quite promptly and respiratory irritation more slowly. According to Sax (1963), repeated exposures to formaldehyde vapors may result in chronic irritation of the eyes, nose, and upper respiratory tract.

A recent report gave the average concentration of formaldehyde in the Los Angeles ambient air at less than 0.15 ppm, much lower than Fassett's reported level of discomfort. However, in simulated atmospheric research, Schuck et al (1960) found that the human eye can detect and respond to as little as 0.01 ppm of formaldehyde. They also observed the same irritation intensity in most subjects exposed to concentrations of 0.05 and of 0.5 ppm.

In a study of the photo-oxidation of hydrocarbons, researchers at Stanford Research Institute found that formaldehyde and acrolein accounted for the majority of the eye irritation produced by photochemical products, but the concentrations of these aldehydes required to produce eye irritation were much in excess of measured atmospheric concentrations. For example, again in the Los Angeles ambient air, only about 0.02 ppm of acrolein was found. Smith (1962) states that concentrations of acrolein of 0.25 ppm can cause moderate irritation of the eyes and nose in exposures as short as 5 minutes. Fassett (1963) reports no known cases of chronic toxicity, but Sax (1963) says that inhalation may cause an asthmatic reaction and that repeated skin contact may produce chronic irritation and dermatitis.

In animal experimentation the effects of exposure to low concentrations of both formaldehyde and acrolein were found to be reversible when the animals were returned to clean air.

Fassett (1963) provides a tabulation of the toxicity of aldehydes to animals via inhalation (Table IV-2).

The information and data provided in the literature indicate that aldehydes constitute little, if any, threat to health at concentrations found in ambient air, but rather are noticeable irritants. Before it can be stated with certainty, however, such a conclusion must be supported by data obtained both in emission inventories and in long-term low-level exposures. A recent literature review concerning aldehydes (Stahl, 1969) covers the subject reasonably comprehensively and cites the same gaps in available information as stated above.

5. Aromatics

Lonneman, et al (1968) collected 126 samples in downtown Los Angeles over a 26-day period from about 7:00 A.M. to 3:00 P.M. to determine aromatic hydrocarbon concentrations. The average concentration of total aromatics was 0.106 ppm by volume, the highest reading being 0.33 ppm.

TABLE IV-2 - TOXICITY OF ALDEHYDES TO ANIMALS VIA INHALATION

Compound	Species	ppm	Time,hr	Mortality
Saturated Aliphatic Aldehydes				
Formaldehyde	Rat	250	4	LC_{50}[a]
	Rat	815	0.5	LC_{50}
	Cat	650	8	LC_{50} approx
	Cat	200	3.5	All survived
Acetaldehyde	Rat	Sat vap[b]	2 min	LC_{100}[d]
	Rat	16,000	4	0/6
	Rat	20,000	30 min	LC_{50}
	Cat	13,600	0.25	1/1
	Cat	4,100	3-5	0/1
	Cat	256	5	0/1
Propionaldehyde	Rat	8,000	4	5/6
	Rat	60,000	0.3	3/3
	Rat	26,000	0.5	LC_{50}
Ethoxypropionaldehyde	Rat	500	4	6/6
αβ-Dichloropropionaldehyde		Concd vap[c]	2 min	6/6
	Rat	16	4	4/6
n-Butyraldehyde	Rat	8,000	4	1/6
	Rat	60,000	0.5	LC_{50}
Isobutyraldehyde	Rat	8,000	4	1/6
β-Hydroxybutyraldehyde (aldol, acetaldol)	Rat	4,000	4	2/6
	Rat	Sat vap	0.5	No deaths
n-Valeraldehyde	Rat	48,000	1.2	3/3
	Rat	1,400	6	0/3
2-Methylbutyraldehyde	Rat	67,000	0.3	3/3
	Rat	3,800	6.0	0/3
	Rat	1,043	6.0	0/3
n-Hexaldehyde (hexanal)	Rat	Concd vap	4	0/6
	Rat	2,000	4	1/6
2-Ethylbutyraldehyde	Rat	Concd vap	5 min	0/6
	Rat	8,000	1	5/6
2-Ethylhexyladehyde (α-ethylcaproaldehyde)	Rat	25,000	13 min	3/3
	Rat	4,000	4	1/6
	Rat	2,000	23 min	3/3
	Rat	145	6	0/3

Table IV-2 (Continued)

Compound	Species	ppm	Time,hr	Mortality
Unsaturated Aliphatic Aldehydes				
Acrolein	Rat	8	4	1/6
	Cat	690-1,150	2	3/3
	Cat	18-92	3-4	0/2
	Cat	11	3-10	0/2
	Rat	130	30 min	LC_{50}
Methacrylaldehyde (Methacrolein)	Rat	250	4	5/6
2-Ethyl-3-propyl acrolein	Rat	Concd vap	8	0/6
Crotonaldehyde (β-methyl acrolein)	Rat	Concd vap	1 min	0/6
	Rat	1,400	30 min	LC_{50}
Methyl-β-ethyl acrolein (2-methyl-2-penten-1-al)	Rat	2,000	4	3/6
Aliphatic Dialdehydes				
Succinaldehyde (25% in H_2O)	Rat	Concd vap (ca. 15,000 ug/liter)	6	0/3
Hexa-2,4-dienal	Rat	2,000	4	1/6
3-Methyl glutaraldehyde	Rat	Concd vap	8	0/6
	Rat	Concd vap	6	0/3
α-Hydroxyadipaldehyde	Rat	Concd vap	8	0/6

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[a] LC_{50} = Lethal concentration at which 50% mortality is observed

[b] Sat vap = Saturated vapor

[c] Concd vap = Concentrated vapor

d = fraction denotes deaths per number of subjects

Benzene, toluene, and the xylene isomers made up 0.082 ppm of the average of 0.106 ppm, or 77 percent of the total aromatics measured. Toluene was the single most abundant aromatic hydrocarbon, with concentrations about twice as high as either benzene or m-xylene, the next highest. The remaining 23 percent of the total aromatic fraction consisted of ethylene; ethyl toluenes; trimethyl-propyl-, and butyl-benzenes; and other unidentified higher homologs.

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended 200 ppm as the threshold limit value for toluene, an acceptable limit for exposures not exceeding 8 hours daily. Von Oettingen (1940) reports that at 200 ppm subjects experience a slight but definite impairment of coordination and a slowing of reaction time, suggesting that a lower limit might be desirable.

Chronic benzene poisoning results from repeated or continuous exposure to relatively low concentrations of benzene vapor. The level and degree of exposure necessary to produce poisoning vary widely. There are at least two well-authenticated cases of poisoning by repeated exposures to 75 ppm. Inhalation of 50-150 ppm of benzene for 5 hours caused slight headache, weariness, and lassitude (API, 1960).

Benzene is relatively insoluble in body fluids and tissues. Practically complete elimination of benzene from the blood occurs within a few minutes after exposure is terminated. Benzene is eliminated from the body via the lungs and the kidneys.

The ACGIH recommended threshold limit value for benzene is 25 ppm for an 8-hour daily exposure.

Chronic exposure to xylene may produce symptoms similar to those of chronic toluene poisoning. There may be systemic symptoms indicating nervous system involvement. Serious blood changes are not usually encountered. Experimental subjects exposed to various concentrations of xylene considered 100 ppm the highest concentration tolerable for an 8-hour exposure (API, 1960).

The ACGIH recommended threshold limit value for xylene is 100 ppm for an 8-hour daily exposure.

Here again, with aromatics as with aldehydes, one finds a paucity of data on low-level exposures. It appears that community levels such as measured in the Los Angeles Basin present no cause for concern regarding health hazards, but additional information is required to substantiate a definitive statement in this regard.

Table IV-3 provides comparative effects of acute and chronic exposures to aromatic hydrocarbon vapors in air (API, 1960).

6. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons are universally present in the atmosphere (Coffin, 1971; Sawicki, et al, 1960; Heimann, 1967; Katz, 1962). A quantitative tabulation of the polycyclic aromatic hydrocarbon (PAH) content of the air of 14 American cities is presented in Table IV-4. The stability of PAH is consistent with their survival in the atmosphere for sufficient periods of time to be respired by the general population (Falk et al, 1956).

The literature on PAH emissions shows that they are products of incomplete combustion of carboniferous fuels and evaporation of coal-tar pitch products (Coffin, 1971; Sawicki, 1962a; Faith, 1960). Qualitative identification of PAH was made in stack gases from pulp mills; in the air surrounding iron and steel works, heat generation, and incineration processes; and in the fumes from coal-tire pitch operations (Hendrickson et al, 1963; Tanimura, 1968; Hangebrauck et al, 1964; Sawicki et al, 1962b).

A nationwide inventory in 1968 of air pollutant emissions showed that industrial process losses accounted for 4.6 million tons of the approximately 32 million tons of hydrocarbons emitted annually in the United States (USDHEW, 1970). Of this national total, 60 percent was emitted in urban areas. Higher concentrations of PAH in urban areas have been verified worldwide. In addition to variances in PAH concentrations in urban and rural areas, differences in PAH levels also stem from geographic location and climatic conditions. PAH concentrations are generally greater in winter, possibly because of seasonal differences in fuel use practices and combustion efficiency (Sawicki et al, 1962a). The benzo(α)pyrene content of particulate air pollutants also differs markedly in eastern and western cities, the western cities showing much lower concentrations (Katz, 1962).

Some polynuclear aromatic hydrocarbons exhibit carcinogenic activity, i.e., chrysene, benz(α)pyrene, benzo(e)pyrene, and benzo(g,h,i)perylene. Of these, benzo (α)pyrene is the strongest carcinogen as well as the most stable. Numerous experimental studies on rats and mice have demonstrated a possible carcinogenic hazard related to some pollutants in the atmosphere. Numerous investigators

TABLE IV-3 - Comparative Effects of Acute and Chronic Exposures to Aromatic Hydrocarbon Vapors in Air

Compound	Subject	Concentration ppm	Concentration mg/m^3	Daily Exposure, hr	Exposure, days	Effect
Benzene	Man	25	80	Acute*	--	Threshold limit value (TLV)
	Man	100	319	Acute	--	Mucous membrane irritation
	Mice	370	1,180	Acute	--	Threshold for affecting the central nervous system
	Man	3,000	9,570	Acute	--	Endurable for 1/2-1 hour
	Mice	4,700	14,993	Acute	---	Prostration
	Mice	7,400	23,606	Acute	--	LC_{50}
	Man	7,500	23,925	Acute	--	Dangerous after 1/2-1 hour
	Mice	14,100	44,979	Acute	--	LC_{100}
	Rats	17,800	56,782	Acute	--	LC_{100}
	Man	20,000	63,800	Acute	--	Fatal after 5-10 minutes
	Man	50-100	188-377	Acute	--	No effect
Toluene	Man	200	753	8	1	Mild fatigue, weakness, confusion, skin parethesias
	Man	300	1,130	8	1	Symptoms more pronounced
	Man	400	1,506	8	1	Also: mental confusion
	Man	600	2,259	3	1	Also: nausea, headache, dizziness
	Man	600	2,259	8	1	Also: loss of coordination, staggering gait,pupils dilated
	Mice	2,700	10,166	Acute	--	Prostration
	Mice	6,700	25,226	Acute	--	LC_{50}
	Mice	9,500	35,768	Acute	--	LC_{100}
	Rat	13,500	50,828	Acute	--	LC_{100}
Styrene	Man	100	418	Acute	--	Threshold limit value (TLV)
	Guinea pig	650	2,714	8	180	No effect
	Rat	1,300	5,428	8	180	Eye and nasal irritation only
	Rabbit	1,300	5,428	8	180	Eye and nasal irritation only
	Guinea pig	1,300	5,428	8	180	10% deaths
	Guinea pig & rat	2,500	10,438	8	1	Some fatalities; varying degree of weakness, stupor, incoordination, tremor, unconsciousness (in 10 hrs)
	Guinea pig & rat	5,000	20,875	1	1	Unconsconsciouness in 1 hour
	Guinea pig & rat	10,000	41,750	1/2-1	1	Unconsciousness in 10 minutes; deaths in 30-60 minutes
Xylene	Mice	174	755	Acute	--	Threshold for affecting central nervous system
	Man	200	868	Acute	--	Threshold limit value (TLV)
	Rat & Rabbit	690	2,995	8	130	No hematological effects
	Rabbit	1,150	4,991	8	55	Decreased leukocytes and red blood cells; increased platelets
	Mice	4,699	20,394	Acute	--	Prostration
	Mice	9,200	39,928	Acute	--	LC_{50}
	Mice	12,650	54,901	Acute	--	LC_{100}
	Rat	17,250	74,865	Acute	--	LC_{100}

*Acute refers to a single short term exposure, not repeated

Table IV-4 - Polycyclic Hydrocarbon Content of the Air for Selected Cities

City Winter, 1959 (ug/1000 m3)	Month	BghiP*	BaP	BeP	BkF	P	Cor	Per	Anth	Total
Atlanta	Feb.	8.9	7.4	4.7	6.0	6.0	4.3	1.1	0.52	38.92
Birmingham	Feb.	18.0	25.0	10.0	13.0	17.0	3.5	5.5	2.2	94.2
Detroit	Feb.	33.0	31.0	23.0	20.0	25.0	6.4	6.0	2.0	146.4
Los Angeles	Feb.	18.0	5.3	8.1	5.7	6.0	12.0	1.6	0.16	56.86
Nashville	Jan.	17.0	25.0	14.0	15.0	3.0	4.6	4.4	1.8	111.8
New Orleans	Feb.	7.3	4.1	6.4	3.9	2.3	27.0	0.8	0.10	27.6
San Francisco	Jan.	7.5	2.3	2.9	1.7	1.9	4.9	0.34	0.10	21.64
Seattle	Jan.-Mar.	14.0	9.0	---	8.1	6.7	15.0	2.4	1.0	56.2
Sioux Falls	Jan.-Mar.	8.3	4.0	---	2.7	4.0	3.7	0.82	0.22	23.74
South Bend	Jan.-Mar.	12.0	16.0	14.0	10.0	32.0	4.7	3.0	1.5	93.2
Wheeling	Jan.-Mar.	14.0	21.0	---	13.0	22.0	3.8	2.6	1.4	77.8
Youngstown	Jan.-Mar.	22.0	28.0	---	18.0	34.0	3.4	7.4	3.4	116.2

*BghiP = Benzo(g,h,i)perylene; BaP = Benzo(a)pyrene; BeP - Benzo(e)pyrene: BkF = Benzo(k) fluoranthene; P = Pyrene; C = Coronene; Per = Perylene; Anth = Anthanthrene

Sawicki, 1962a

extracted tarry substances from air pollutants, and by employing a "skin painting" method on mice, produced tumors which they attributed to the benzo(α)pyrene content (Shabad, 1960; Sawicki et al, 1962a; Gurinov et al, 1969). Thus far, experimental production of long tumors by inhalation methods in C57 black mice has been unsuccessful. A reason postulated for this discrepancy is that carcinogenic hydrocarbons are biologically ineffective when adsorbed on soot particles within a given size range, becoming effective only upon elution or displacement from the soot particles. The sebaceous secretions on the skin may provide the liquid solvent to elute the carcinogenic hydrocarbons from soot, while in the lungs no such eluting agent is present.

It has been further postulated (Katz et al, 1954) that if gasoline vapors are simultaneously inhaled they may act as elements which extract the carbinogenic hydrocarbons from the soot so as to allow them to act on the respiratory mucosa. Both Saffiotti et al (1965) and Gross et al (1969) induced lung tumors in small laboratory animals with carcinogens adsorbed on hematite (iron oxide, Fe_2O_3). Inhalation experiments conducted on mice (Gardner et al, 1970) exposed to both ambient and filtered Los Angeles air resulted in no difference in histologic appearance and no increase in incidence in lung tumors;however, prolonged exposure of mice to ambient Los Angeles air suggested increased susceptibility to pulmonary infection.

Concentrated efforts have been directed toward studies of the acute effects of air pollution but apparently not on the long-term effects of exposure to polluted atmospheres. Falk and Kotin (1955) analyzed lungs of typical urban dwellers and recovered approximately one gram of soot (average per dweller). This failed to reveal the usual aromatic hydrocarbons when subjected to spectrophotometric analysis. They attribute the apparent elution of carcinogenic polynuclear aromatic hydrocarbons from soot to intercellular protein activity (Falk et al, 1960; Kotin and Falk, 1959). Even though carcinogenic hydrocarbons have been detected in urban air the literature provides no clear indication that their presence is significant though their interaction with biological and physiological substances might be the mechanisms of carcinogenesis (Anderson, 1967). In reviewing the literature, we found no clear-cut correlations between the effects of pollution by polynuclear aromatic hydrocarbons and production of lung tumors in man.

7. Pollutants Created by Atmospheric Hydrocarbon Reactions

The major concern with regard to health effects of gaseous hydrocarbon emissions is due to their atmospheric interactions to form photochemical smog. Photochemical reactions to form smog are complex but can be generally described as reactions of reactive hydrocarbons with oxides of nitrogen in the presence of ultraviolet radiation.

It is important at this point to differentiate between primary and secondary pollutants. Primary pollutants are those emitted directly into the atmosphere such as the hydrocarbons and oxides of nitrogen; secondary pollutants result from chemical reactions of primary pollutants emitted into the atmosphere and exposed to sunlight. Examples of secondary pollutants are the peroxyacyl nitrates (PAN), ozone, aldehydes, and aerosols (Pitts, 1969). Some pollutants, such as aldehydes, may be either primary or secondary pollutants.

a. Aldehydes - Photooxidation of hydrocarbon-nitrogen oxide mixtures can result in the formation of low molecular weight aldehydes, principally formaldehyde and acrolein (Table IV-5). The effects of aldehydes on humans, previously discussed (Sect. B.4), include the highly irritating effects of formaldehyde and acrolein vapors on the mucous membranes of the eyes, nose, and throat (Fassett,1963; Renzetti and Bryan, 1961). Although concentrations of these two aldehydes are generally higher than those of other aldehydes present in the air, neither substance exists in ambient air in sufficient concentration to account for the degree of eye irritation experienced.

b. Aerosols - Biological and biochemical effects produced with organic aerosols are governed primarily by particle size, which determines their site of deposition, retention, and metabolic fate in human lungs. Ordinarily, particles 10μ or larger are prevented from entering the depths of the lungs because of the filtering action of the upper respiratory tract and its airways. Solubility of particles in water is another factor affecting potential biological effects. Soluble aerosols in adequate concentration may be expected to produce an immediate effect; insoluble particles must first be deposited and retained in the body, later to be acted on by tissue fluids and chemically altered before their effects occur (Hatch and Gross, 1964). Thus, the effects of particulate pollutants may be immediate and acute, as with sulfuric acid mist, or delayed and chronic, as with carcinogens such as the polynuclear aromatic hydrocarbons (Kotin,1964).

Table IV-5 - Aldehyde Yields From Photooxidation of Hydrocarbon-Nitrogen Oxide Mixtures

Moles of Aldehyde per Mole of Hydrocarbon*

Hydrocarbon	Formaldehyde	Acrolein	Aliphatic Aldehydes
Ethylene	0.3-0.4		0.3-0.4
Propylene	0.4		0.6-0.8
1-Butene	0.4		0.65
Isobutene	0.5-0.7		0.5-0.7
Trans-2-butene	0.35		1.25-1.55
1,3-Butadiene	0.3-0.5	0.2-0.3	0.5-0.8
1-Pentane	0.5		1.0
2-Methyl-2-butene	0.3-0.5		0.8-1.2
Cis-2-hexane			0.9-1.0
Toluene	0.05		0.1
Xylenes	0.15-0.2		0.2-0.3
1,3,5-Trimethylbenzene	0.15-0.2		0.2-0.3

*Based on hydrocarbon initially present as reactant.

Altshuller, A.P., Air and Water Poll. Int. J. 10:713-733,1966

Both Saffiotti (1965) and Gross (1969) demonstrated the ability of inert dusts to transport organic pollutants, in these instances polynuclear aromatic hydrocarbons, into the lungs of small laboratory animals by intratracheal administration.

c. Photochemical Oxidants - Of the gaseous pollutants resulting from photochemical reaction, ozone is perhaps the best understood and most abundant. It is formed by a cycle that involves the oxides of nitrogen, atmospheric oxygen and hydrocarbons. The latter allow ozone to accumulate by reacting to scavenge the nitric oxide, which would reduce the ozone (Table IV-7). This process is illustrative of an antagonistic action between two gases (Stephens, 1969; Stokinger, 1968).

Peroxyacyl nitrates (PAN), another important group of oxidants in ambient air, result from reactions between oxides of nitrogen and organic pollutants. PAN has been identified as an effective irritant in simple synthetic photochemical systems; however, it is not present in ambient air in concnetrations high enough to account for the degree of eye irritation experienced (Renzetti and Bryan, 1961). Smith (1965) suggested that exposure to peroxyacyl nitrate results in increased oxygen uptake by human subjects when exposed to the additional stress of exercise. Although substantiative evidence is necessary before any conclusive statement can be made in this regard, exercise has been proscribed in certain communities and schools during "smog alert" situations as a precautionary measure.

Investigation of the biological effects of photochemical oxidants as pollutants is complicated by their atmospheric instability,the necessity of employing unrealistic concentrations to demonstrate biological effects, and finally the extreme difficulty of combining gases quantitatively in attempts to simulate atmospheric conditions (Kotin and Falk, 1964).

Gaseous oxidation reactions constitute one of the most important types of reactions in community atmospheres. Sudden increases in concentrations of oxidants are related to eye irritation. To date, however, we find no good data to indicate whether oxidants, nitrogen dioxide, and/or hydrocarbons at existing community air levels play any role in the causation of respiratory disease. It is difficult to determine the importance of synergistic effects in actual atmospheric conditions since in many cases the individual

Table IV-6 - Atmospheric Reactions of Pollutants With Ozone*

Reaction	Rate (1 ppm of pollutants)
$NO + O_3 \longrightarrow NO_2 + O_2$	Very fast, 170 ppm/h
$NO_2 + O_3 \longrightarrow NO_3 + O_2$	Fast, 0.3-0.6 ppm/h
$SO_2 + O_3 \longrightarrow SO_3 + O_2$	Very slow, <0.001 ppm/h
$H_2S + O_3 \longrightarrow SO_2 + H_2O$	Fast, 2 ppm/h
$CO + O_3 \longrightarrow CO_2 + O_2$	No measurable rate at ambient temperature
Paraffins + $O_3 \longrightarrow$ products	Very slow
Alkylbenzenes + $O_3 \longrightarrow$ products	Very slow, <0.001 ppm/h
Acetylene + $O_3 \longrightarrow$ products	Very slow <0.001 ppm/h
Ethylene + $O_3 \longrightarrow$ products	Slow, 0.02 ppm/h
Propylene + $O_3 \longrightarrow$ products	Slow, 0.07 ppm/h
Olefins with internal double bonds + $O_3 \longrightarrow$ products	Fast, 0.2-2 ppm/h

*Altshuller, 1969

effects of pollutants may be either intensified or are cancelled by interaction. However, no one pollutant can be excluded from consideration because it alone has not been found to produce adverse health effects at a given concentration.

8. Odors and Odorants

Odors may be one of the earliest manifestations of air pollution since some odors are detectable even at extremely low concentrations. Any substance or mixture of substances in the vapor or gaseous phase that stimulates the sensation of smell is an odorant; an odor is defined as the sensation perceived as a result of olfactory stimulus (Duffee, 1968). Whether an odor is considered offensive may depend on prior psychological conditions of the receptor as well as on the nature and strength of the odor.

This brief section in no way represents an exhaustive reservoir of the available literature on odors, but merely intends to include the subject as a part of the atmospheric health complex.

a. Odorant Sources - Offensive odors emanate from a variety of industrial, domestic and natural sources. These odors most frequently reported by city bureaus over several years are listed in Table IV-7, as reported by Kerka and Kaiser (1958). The most offensive odors originate from plants that produce low molecular weight sulfur and nitrogen compounds, such as mercaptans, hydrogen sulfide, ammonia and amines. Major sources frequently reported by city bureaus are animal rendering plants, petroleum refineries, chemical and metallurgical plants, and sewers and sewage treatment plants. Kraft mills are not frequently mentioned, probably due to their location in non-urban areas. On occasion, odors can be detected in a 10 to 20 mile radius from the source (Sullivan, 1969).

b. Characteristics of Odors - The quality of an odor is a subjective characteristic evaluated with descriptive words that associate an odor with familiar materials, i.e., fruity, fishy, rank, etc. The odor qualities of some selected odorants are listed in Table IV-8.

Odor intensity and pervasiveness are generally measured by the response of a selected group of human subjects or "odor panel". Laboratory studies results are generally reported as threshold levels (in ppm) at which the odor is barely perceptible by the human subjects.

Table IV-7 - Most Frequently Reported Odor Sources*

Source of Odor	Number Reported
Animal Odors	
Meat packing and rendering plants	12
Fish oil odors from manufacturing plants	5
Poultry ranches and processing	4
Odors From Combustion Processes	
Gasoline and diesel engine exhaust	10
Coke oven and coal gas odors (steel mills)	8
Poorly adjusted heating systems	3
Odors From Food Processing	
Coffee roasting plants	8
Restaurants	4
Bakeries	3
Paint and Related Industries	
Manufacturing of paint, lacquer, and varnish	8
Paint spraying	4
Commercial solvents	3
General Chemicals Odors	
Hydrogen sulfide	7
Sulfur dioxide	4
Ammonia	3
General Industrial Odors	
Burning rubber from smelting and debonding	5
Odors from dry cleaning shops	5
Fertilizer plants	4
Asphalt odors (roofing and street paving)	4
Asphalt odors (manufacturing)	3
Plastic manufacturing	3
Foundry Odors	
Coke oven odors	4
Heat treating, oil quenching, and pickling	3
Smelting	2

Table IV-7 (Continued)

Source of Odor	Number Reported
Odors From Combustible Waste	
Home incinerators and backyard trash fires	4
City incinerators burning garbage	3
Open-dump burning	2
Refinery Odors	
Mercaptans	3
Crude oil and gasoline	3
Sulfur	1
Odors From Decomposition of Waste	
Putrefaction and oxidation (organic acids**)	3
Organic nitrogen compounds (decomposition of protein**)	2
Decomposition of lignite (plant cells)	1
Sewage Odors	
City sewers carrying industrial waste	3
Sewage treatment plants	2

*Kerka, 1958

**Probably related to meat processing plants

Table IV-8 - Odor Qualities of Selected Odorants*

Compound	Odor Quality
Carbon disulfide	Strong, objectionable
Nitrogen dioxide	Strong, irritating
Ammonia	Ammoniacal
Diethyl amine	Fishy
Triethyl amine	Fishy
Hydrogen sulfide	Rotten eggs
Methyl mercaptan	Skunk
Dimethyl sulfide	Rotten cabbage
Dimethyl disulfide	Rotten cabbage
Phenol	Carbolic disinfectant
Acetic acid	Penetrating; vinegar when dilute
Acrolein	Irritating; snuffed candle
Vanillan	Vanilla
Methyl amine	Ammonia, boiled lobsters
Triethanolamine	Oily; slightly fishy
Thiophene	Faint; neutral
Pyridine	Rank, unpleasant
Indole	Alphanaphthyl amine when concentrated, but jasmine when dilute
Skatole	Fecal

*Moncrieff (1967)

Odor intensity can be defined as a numerical indication of odor strength. The following set of values associated with a numerical scale has been established to allow convenient statistical treatment of odor levels (Turk, 1960; Kerka, 1958; Nader, 1958).

Odorless	0
Threshold (barely perceptible)	1
Definite	2
Strong	3
Overpowering	4

Table IV-9 lists odor threshold values and TLV's of some odorants. The upper odor threshold concentrations reported for some odorants exceed the TLV, indicating that the TLV may be exceeded without some subjects detecting the presence of the odorant via the olfactory senses.

The acceptability or unacceptability of an odor may range from very pleasant to obnoxious, depending upon quality and intensity of the odor and/or prior conditioning of the subject exposed. Odors are best evaluated upon the first and second inhalations because subsequent inhalations tend to fatigue the receptor's sense of smell (Patty, 1948).

Pervasiveness, another significant characteristic of odors, is defined as the "...quality of an odor to pervade a large volume of air and still continue to possess a detectable intensity" (Nader, 1958).

Odor source samples are normally evaluated by odor panels using the technique of successive dilution with clean air until the odor threshold is reached. Results are reported in odor units per unit volume, equivalent to the number of volume dilutions required to reach the odor threshold concentration.

c. Health Effects - The relationship of odors to the health of man is difficult to prove, since odors in themselves do not appear to produce observable pathological (anatomic) effects. No relationship of odors to toxicity has been established; an odor can, however, serve a useful function as a warning of the presence of a toxic substance, as with hydrogen sulfide. Offensive odors, however, have been reported to cause anusea, vomiting, headache, loss of appetite, impaired respiration, insomnia, and mental depression.

Table IV-9 - Recognition Odor Thresholds and TLV's of Some Odorants

Odorant	Odor Threshold(1) (ppm)	TLV(2) (ppm)
Acetaldehyde	.06, .07, .21	200
Acrolein	.21, .33, 1.5, 1.8	0.5
Carbon disulfide	.21, .77	20
Diethyl sulfide	.003, .0059	
Dimethyl amine	.047, 0.6	10
Dimethyl sulfide	.001, .0025, .004, .02	
Ethyl mercaptain	.0004, .001, .002, .0033	2
Formaldehyde	.06-.09, 1.0, 0.4-6.6	5
Gasoline	10	500
Hydrogen sulfide	.01, .0011, 0.13-1.0	20
Methyl mercaptain	.00099, .0021, .0011, .04	2
Nitrogen dioxide	4.0, 1-3	5
Ozone	.005, .02-.05, 0.1, 0.5, 2.0	0.1
Skatole	.000000075, .019	
Sulfur dioxide	.03-1.0, 0.47, 3.0	5
Thiopene	.00077	

(1) Taken from various reference sources by R. Sullivan (1969).

(2) Documentation of Threshold Limit Values, copyright 1966, by American Conference of Governmental Industrial Higienists

Surveys have indicated that the general public almost invariably links air pollution with "bad" smells. Because of the subjectivity of odor complaints, as shown in opinion surveys, the level of air pollution cannot be objectively appraised on the basis of complaints of bad smells.

Some allergic conditions, such as asthma attacks, may be related specifically to odors (Horesh, 1966; Urbach, 1942).

C. PHOTOCHEMICAL SMOG

1. Introduction

Photochemical smog is a term that describes the manifestations of the complex photochemical reactions of atmospheric pollutants. The photochemical reactions that produce photochemical smog can involve a variety of reactants, both organic and inorganic, but it has been recognized for many years that hydrocarbons in general are essential reactants for smog formation. However, individual hydrocarbon species differ greatly in their relative reactivities and in their production of the manifestations of smog such as eye irritation, visibility reduction, and plant damage.

A considerable body of literature describes various aspects of the reaction mechanisms, reaction kinetics, and characteristics of photochemical smog. Several comprehensive reviews have been written on the photochemical reactions involved in smog formation (Leighton, 1961; Altshuller and Bufalini, 1965, 1971; System Development Corporation, 1970). Much of the existing data on photochemical systems has been reviewed and evaluated in the Air Quality Criteria for Photochemical Oxidants, AP-63, and the Air Quality Criteria for Hydrocarbons, AP-64.

The recognized variability of individual hydrocarbons and chemical group classifications in their contribution to photochemical smog formation requires that some relative measure of this variability be developed in order to determine which hydrocarbons should be controlled. The following sections describe the development of relative measures of smog contribution which were used to rank the major source emissions.

2. Photochemical Reactivity

Photochemical reactivity is the tendency of a particular substance to participate in photochemical reactions and produce the adverse manifestations associated with smog. As with most chemical reactions, photochemical reactivity is a function of chemical structure and is additionally inlfuenced by specific reaction conditions. The extremely complex and uncontrollable nature of ambient atmospheres has influenced investigators to employ simulated and simplified reaction conditions in studies of photochemical reactivity. The laboratory conditions employed for photochemical reaction studies vary widely, but they usually involve some form of simulated atmosphere, generically termed a "smog chamber".

Hydrocarbon reactivity studies in the laboratory have developed considerable information on the relative reactivities of various homologous series and of specific compounds. The usefulness of much of this information, however, is highly questionable. Reaction conditions and techniques used to measure reactivity vary widely, and thus the number of hydrocarbons investigated by any one consistent approach has been limited. Additionally, the degree of simulation of ambient atmospheric conditions has often been quite poor and thus it has not been apparent how much of the data can be extrapolated to actual atmospheric smog formation.

Recent investigative trends are being directed toward reactivity studies of ambient atmospheric samples, so that in the near future data more directly applicable to real conditions may be available.

Laboratory or smog chamber data available for assessment of relative hydrocarbon reactivities include hydrocarbon consumption, nitric oxide oxidation, ozone or oxidant* formation, and eye irritation. The various investigators and reviewers have generally attempted to rank the hydrocarbon investigated on reactivity scales which use one or more of the above measurement parameters.

3. Reactivity Scales

In their reviews of the literature data on photochemical aspects of air pollution, Altshuller and Bufalini (1965, 1971) compared reactivity data obtained by various investigators. Altshuller (1966a) summarized available reactivity data and considered the problems involved in developing a single index of reactivity for organic substances.

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*The term "oxidant" is generally defined as that group of reaction products that will oxidize potassium iodide.

Hydrocarbon consumption and nitric oxide formation have been widely used as measures of relative hydrocarbon reactivity in smog chamber studies. Despite differences in reaction conditions and measurement techniques, the relative ordering of hydrocarbon group classifications by these measures is fairly consistent. The relative ordering by hydrocarbon consumption from laboratory measurements has also been shown to be consistent with that obtained by irradiation of ambient atmospheric samples.

Relative reactivities based on hydrocarbon consumption and nitric oxide oxidation do, however, show significant differences when attempts were made to quantify reactivity relationships. Investigators have generally developed reactivity scales by choosing an arbitrary scale, such as 0 to 2 or 0 to 10, and assigning the highest scale number to the most reactive compound or group investigated. Other compounds are then assigned a scale number in relation to their reactivity relative to the highest ranking compound. Altshuller (1971) compared the results of several studies in this fashion, as shown in Tables IV-10 and IV-11. Table IV-11 also includes data from the more recent studies by Glasson and Tuesday (1970) and Levy and Miller (1970) which were not included in Altshuller's review. In these tabulations, differences in scaling used by the original investigators were adjusted to permit direct comparison. This was done by assignment of the same scale number to one compound common to the studies being compared and adjusting other scale numbers in a manner consistent with the original ordering.

Glasson and Tuesday (1970) investigated nitric oxide oxidation rates of a large number of hydrocarbons under a standard set of conditions and demonstrated that reactivity ordering according to hydrocarbon class requires rather detailed breakdown of hydrocarbon classes into specific structural groupings. To avoid extreme overlapping of reactivity between groups or structural classes, six structural classes were required. Table IV-12 shows the structural or reactivity classes and their relative reactivities on a 0 to 100 scale, as summarized by Glasson and Tuesday.

Reported relative reactivity rankings based on oxidant formation and eye irritation data show much less internal agreement than those based on hydrocarbon consumption or nitric oxide oxidation. Oxidant formation is highly dependent on irradiation times and hydrocarbon to nitrogen oxides ratio and thus there are significant variations in reported data.

Eye irritation data depend on human subject response and may thus be subjective and unreliable. Additionally, the chemical factors resulting in eye irritant production are

Table IV-10 - Ranking of Reactivities of Hydrocarbons When Photooxidized in Presence of Nitrogen Oxides Under Static Conditions

Hydrocarbon	Schuck & Doyle (1959)	Stephens & Scott (1969)	Tuesday (1963)
Tetramethylethylene	10	10	10
trans-2-Butene	6		8
cis-3-Hexene		6	
Isobutene	1.5	2	2
1,3-Butadiene	1		
Propylene	1	2	1
m-Xylene		1	
p-Xylene	0.5	0.5	
Ethylene	0.1	0.3	
Hexanes, octanes	<0.1		
Pentanes	<0.01		

Table IV-11 - Reactivities of Hydrocarbons Based on Ability to Participate in Photooxidation of Nitric Oxide to Nitrogen Dioxide(a)

	Ranking			
	Altshuller and Cohen	Glasson and Tuesday		Levy and Miller
Hydrocarbon	(1963)	(1965)	(1970)	(1970)
2,3-Dimethylbutene-2		10		
2-Methyl-2-butene		3		
trans-2-Butene	2(a)	2	2	2
Isobutene	1			
Propylene	1	0.5	0.6	
Ethylene	0.4	0.3	0.3	0.6
1,3,5-Trimethylbenzene	1.2	1.2	0.9	
m-Xylene	1	0.9	0.7	0.6
1,2,3,5-Tetramethylbenzene	0.9	0.7		
1,2,4-Trimethylbenzene	0.6	0.7	0.6	
o-and p-Xylene	0.4	0.4	0.4	
o- and p-Diethylbenzene	0.4	0.4		
Propylbenzenes	0.3	0.2		
Toluene	0.2	0.2	0.2	0.2
Benzene	0.15	0.04	0.05	0.03
n-Nonane	0.15			
3-Methylheptane	0.15			
n-Heptane		0.2		
Methylpentanes	<0.1	0.2	0.2	
Pentanes		0.2		
2,2,4-Trimethylpentane	0.15	0.15		
Butanes		0.1		
Ethane		0.03	0.03	
Methane		<0.01		
Acetlyene	0.1			

(a)Arbitrarily adjusted to the same ranking as trans-2-butene on Glasson and Tuesday's scale to permit comparison of other hydrocarbons.

Table IV-12 - Hydrocarbon Reactivity in Nitric Oxide Photooxidation

Hydrocarbons in Reactivity Class	Reactivity Class	Relative Reactivity
Internal olefins with two double bond substitutions	6	100
Cyclopentenes Internal olefins with one double bond substitution	5	40
Internal olefins without double bond substitution	4	15
Cyclohexenes Tri- and tetraalkylbenzenes Diolefins		
Terminal olefins Dialkylbenzenes	3	5
Monoalkylbenzenes C_4 + paraffins	2	2
2,2-Dimethylpropane Propane Benzene Ethane Methane	1	0

apparently unrelated to the other parameters used for reactivity measurement. Heuss and Glasson (1968), in their study of 25 hydrocarbons, found no correlation between eye irritation and chemical measurements of reactivity. A correlation was observed, however, between hydrocarbon structure and eye irritation.

Altshuller (1971) presented a tabulation of relative reactivity, on a 0 to 10 scale, based on eye irritation measurements. This tabulation is shown in Table IV-13.

A program carried out for the National Paint, Varnish and Lacquer Association (Levy and Miller, 1970) examined the reactivity of 45 organic solvents in terms of eye irritation measurements, chemical reactivity, and product yield. The study found poor coorelation between eye irritation response times and any chemical parameters measured.

4. Composite Reactivity Scales

The general lack of correlation of biological response, measured by eye irritation, with other laboratory reactivity measurements has been used as the basis for the agruement that rankings of hydrocarbons should not be based solely on chemical parameters. Altshuller (1966b) suggested that a composite reactivity scale that included biological response as well as chemical measurement of reactivity would be more meaningful than a reactivity scale based on chemical reactivity alone.

This is based on the fact that, in actual smog episodes, eye irritation is the most commonly noted adverse effect on humans. Thus, estimates of relative smog contribution should include some measure of this adverse health effect.

Table IV-14 shows Altshuller's tabulation of chemical group classifications ranked on a 0 to 10 scale according to various chemical and biological response parameters.

For our study,published photochemical reactivity scales were combined to give a Composite Reactivity Index for a variety of individual hydrocarbon compounds. This Index ranking, shown in Table IV-15 was based on a scale of 0 to 10, since this scale allows a reasonable range for dispersion of high to low reactivity without implying undue precision in the placement of individual compounds relative to others with similar structural characteristics.

Table IV-13 - Eye Irritation Reactivity*

Hydrocarbon	Eye Irritation Reactivity	Hydrocarbon	Eye Irritation Reactivity
n-Butane	0	m-Xylene	2.9
n-Hexane	0	1,3,5-Trimethylbenzene	3.1
Isooctane	0.9	---	---
tert-Butylbenzene	0.9	1-Hexene	3.5
Benzene	1.0	Propylene	3.9
Ethylene	1.0	Ethylbenzene	4.3
1-Butene	1.3	Toluene	5.3
Tetramethylethylene	1.4	n-Propylbenzene	5.4
cis-2-Butene	1.6	Isobutylbenzene	5.7
Isopropylbenzene	1.6	n-Butylbenzene	6.4
sec-Butylbenzene	1.8	1,3-Butadiene	6.9
2-Methyl-2-butene	1.9	α-Methylstyrene	7.4
trans-2-Butene	2.3	Alkylbenzene	8.4
o-Xylene	2.3	β-Methylstyrene	8.9
p-Xylene	2.5	Styrene	8.9

*Altshuller(1971)

Table IV-14 - Comparison of Product Yields and Effects Caused by Various Organics

Substance or Sub-Class	Respone on 0 to 10 Scale Ozone or Oxidant	Peroxy-acyl Nitrate	Formal-dehyde	Aerosol	Eye Irrita-tion	Plant Damage	Averaged Response
C_1-C_5 paraffins	0	0	0	0	0	0	0
acetylene	0	0	0	0	0	0	0
benzene	0	0	0	0	0	0	0
C_6+ paraffins	0-4	0	0	0	0	0	1
toluene (and other monoalkylbenzenes)	4	ND(a)	2	2	4	0-3	3
ethylene	6	0	6	1-2	5	+(b)	4
1-alkenes	6-10	4-6	7-10	4-8	4-8	6-8	7
diolefins	6-8	0-2	8-10	10	10	0	6
dialkyl and trialkyl-benzenes	6-10	5-10	2-4	+(b)	4-8	5-10	6
internally double-bonded olefins	5-10	8-10	4-6	6-10	4-8	10	8
aliphatic aldehydes	5-10	+(b)	+(b)	ND(a)	+(b)	+(b)	-

(a) No experimental data available

(b) Effect noted experimentally but data insufficient to quantitate.

Table IV-15 - Composite Reactivity Index Values For Selected Hydrocarbons

Compound	Composite Reactivity Index (0 to 10 scale)
2-Butene,2,3-dimethyl	10
2-Pentene,2,3-dimethyl	9
2-Butene, trans-	8
2-Butene, cis-	8
1-Butene, 2-methyl-	8
1-Butene, 3-methyl-	8
2-Butene, 2-methyl-	8
2-Hexene, cis-	8
2-Hexene, trans-	8
3-Hexene, cis-	8
3-Hexene, trans-	8
2-Pentene	8
2-Pentene, cis-	8
2-Pentene, trans-	8
2-Pentene, 4-methyl-	8
1-Butene	7
1-Hexene	7
Formaldehyde	7
Isobutylene	7
1-Pentene	7
1-Pentene, 2-methyl-	7
1-Pentene, 4-methyl-	7
Propylene	7
Propylene Oxide	7
Styrene	7
Vinyl acetate, monomer	7
Vinyl chloride, monomer	7
O-Xylene	7
m-Xylene	7
p-Xylene	7
Benzene, 1,2,4-trimethyl-	6
Benzene, 1,3,5-trimethyl-	6
1,3-Butadiene	6
Butane, 2-methyl-	6
Cumene	6
Cyclopentane	6
Isobutyl methyl ketone	6
Propadiene	6
Toluene	6
Toluene, diisocyanate	6
Toluene, m-ethyl-	6
Toluene, p-ethyl-	6
Trichloroethylene	6

Table IV-15 (Continued)

Compound	Composite Reactivity Index (0 to 10 scale)
Ethylene	5
Ethyl benzene	4
Cyclohexane	3
Cyclohexanone	3
Cyclopentane	3
Cyclomethyl	3
Ethyl methyl ketone	3
Hexanol, 2-ethyl	3
Isopropyl alcohol	3
Methyl alcohol	3
n-Butyl alcohol	3
Acetone	2
Butyl acetates, mixed	2
Ethyl acetate	2
Ethyl alcohol	2
Benzene	1
Butane, 2,2-dimethyl	1
Butane, 2,3-dimethyl	1
Hexane	1
Hexane, 2-methyl-	1
Hexane, 3-methyl-	1
Pentane, 2,3-dimethyl-	1
Pentane, 2,4-dimethyl-	1
Pentane, 2,-methyl-	1
Pentane, 3,-methyl-	1
Pentane, 2,2,4-trimethyl-	1
Acetylene	0
Butane	0
Cellulose acetate	0
Diethylene glycol	0
Ethane	0
Ethylene dichloride	0
Isobutane	0
Isopentane	0
Methane	0
Methane, trichlorofluoro	0
Methyl chloride	0
Methylene chloride	0
Peptane	0
Propane	0
Perchloroethylene	0

In developing the Composite Reactivity Index, the adverse effects of smog were heavily weighted by basing our scale on that given by Altshuller (1966b) for relative reactivity averaged from product yields and biological response data (Table IV-14).

In order to incorporate reported reactivity data which employed different scaling, e.g., the data of Levy and Miller (1970) which were originally ranked on a scale of from 1 to 3, the reactivities were adjusted to the 0 to 10 scale by assignment of a value of 8 (Altshuller's averaged response) to internally double bonded olefins. Other compounds were then assigned values on the 0 to 10 scale relative to the internally double bonded olefins, consistent with the relative chemical group arrangement of Table IV-14.

5. Chlorinated Hydrocarbon Solvents

Few specific studies have been made of the chlorinated hydrocarbons, with the exception of trichloroethylene. Thus, we estimated the reactivities to the saturated chlorinated compounds to be similar to those of other saturated hydrocarbons.

Altshuller (1971) cited the results of an unpublished study by Kopczynski (1968) of trichloroethylene that included determination of NO_2 formation rate, oxidant formation rate, and eye irritation response. On the basis of chemical reactivity, trichloroethylene was found to be between propylene and ethylene; on the basis of eye irritation manifestations it was somewhat higher than propylene.

Wilson et al, in their study of trichloroethylene, reported both chemical reactivity and eye irritation manifestations to be lower than those observed by Kopczynski. Chass (1970) took exception to certain of the results reported by Wilson, on the basis of differences in experimental procedure and data interpretation, citing results of Los Angeles APCD studies more nearly in agreement with Kopczynski. Chass' interpretation places trichloroethylene in the reactivity range of xylenes and olefins.

We used the data of Kopczynski to assign trichloroethylene a reactivity of 6 on our 0 to 10 relative index.

6. Atmospheric Relationships

Schuck et al (1970) investigated the relationship of ambient air hydrocarbon concentration to smog manifestations by a compilation and correlation of air monitoring data. An empirical relationship was developed by comparision of data from the Continuous Air Monitoring Project (CAMP) for 6:00-9:00 A.M. average non-methane hydrocarbon concentrations with total oxidant concentration levels attained later in the same day. Although only limited data were available for the correlation, a relationship was observed which served to define the upper limit of daily oxidant concentration as a function of the 6:00-9:00 A.M. non-methane hydrocarbon levels. The conclusion from the correlation was that if maximum 1-hour oxidant concentration is to be limited to about 0.1 ppm, the 6:00-9:00 A.M. non-methane hydrocarbon concentrations must be less than about 0.3 ppm (as carbon). This approximately 3:1 relationship was used in the development of ambient air quality standards for hydrocarbons set by the Federal Government (Federal Register 36, 8186, 1971).

D. VEGETATIVE DAMAGE

1. Introduction

Vegetative damage has long been recognized to result from exposure of growing plants to specific hydrocarbons, notably ethylene. More recently, vegetative damage was one of the early manifestations observed in studies of photochemical smog and its effects. As early as 1913, Knight and Crocker (1913) suggested that ehtylene, and perhaps other carbon containing gases, be considered phytotoxic. Haagen-Smit et al (1952) observed damage to sensitive plants from exposure to synthetic smog products.

A review of the literature indicated that plant damage from exposure to ambient atmospheric concentrations of hydrocarbons results predominantly from ethylene and the photochemical smog products. Other inuurious hydrocarbons, such as the aldehydes and unsaturated hydrocarbons other than ethylene, produce plant damage only at concentrations much higher than are present in ambient atmospheres.

2. Relative Importance of Hydrocarbons Causing Plant Damage

Various investigators have studied the relative importance of hydrocarbons in terms of their damage effects on sensitive plant species. General reviews of the effects of hydrocarbons on vegetation have been given by Crocker (1948), Slayton and Platt (1967), and the Air Quality Criteria for Hydrocarbons (USDHEW, 1970).

Specific studies and results are discussed in the following subsections: unsaturated hydrocarbons; aldehydes; and photochemical smog products.

a. Unsaturated Hydrocarbons - Abeles and Gahagen (1967) investigated the effects of exposure of sensitive plants to various concentrations of ethylene, propylene, acetylene, 1-butene, and 1,3-butadiene. They found that exposure to 0.1 ppm ethylene resulted in about one-half maximum abscission. These authors then compared their results with those of other studies (Burg and Burg, 1962; Crocker, 1934; Zimmerman, 1935) as shown in Table IV-16. This tabulation shows the relative concentrations of several unsaturated hydrocarbons that produce the same degree of biological response as ethylene.

Crocker (1935) found that exposure to concentrations of 0.1 ppm ethylene produced epinasty in sensitive plant species. Saturated hydrocarbons, 1,3-butadiene, and benzene ring compounds were found to have no harmful effects under the conditions studies.

Burg and Burg (1962) found that exposure to 0.1 ppm ethylene inhibited elongation of peas. Methane, cis-2-butene, trans-2-butene, and isobutene were inactive.

Dosage-response data from various investigators on the effects of ethylene were summarized in the Air Quality Criteria for Hydrocarbons. Damage to the more sensitive plants, such as orchids, has been observed from exposure to less than 0.1 ppm for as little as 1 hour.

The literature data thus show that, of the unsaturated hydrocarbons, only ethylene produces significant plant damage at low concentrations comparable to those attained in ambient atmospheres. Additionally, the more limited investigation of other simple hydrocarbons indicates that paraffins and benzene ring compounds have no harmful effects on vegetation.

Stephens and Burlesen (1967) and Stephens et al (1967) reported that ambient concentrations of ethylene in congested urban areas were 25-150 $\mu g/m^3$ (0.02-0.13 ppm), well within the harmful range of ethylene.

Table IV-16 - Relative Concentrations of Some Unsaturated Hydrocarbons That Produce Biological Response Similar to that Produced by Ethylene

Compound	Abscission	Epinasty	Inhibition of Growth Pea Stem	Inhibition of Growth Tobacco
Ethylene	1	1	1	1
Propylene	60	500	100	100
Acetylene	1,250	500	2,800	100
1-Butene	100,000+	500,000	270,000+	2,000
1,3-Butadiene	100,000+	---	5,000,000+	---

b. Aldehydes - Haagen-Smit et al (1952) found that exposure to relatively high concentrations of aldehydes resulted in significant damage to sensitive plants. They concluded, however, that no damage should be expected from exposure to atmospheric concentrations of aldehydes.

Investigation of the effects of smog products on vegetation indicated that exposure to formaldehyde and acetaldehyde did not result in plant injury (Stephens, 1961; Altshuller and Hindawi, 1964; Altshuller, 1966).

Brennan (1964) reported that plant injury correlated with total atmospheric aldehydes, but the work was criticized by Hindawi and Altshuller because of poor analytical procedures.

c. Photochemical Products - Harmful effects to vegetation from exposure to photochemical smog products are generally attributed to the oxidant products; ozone, peroxyacetyl nitrate (PAN), and other homologs of PAN. As noted by Lacasse and Moroz (1969), PAN and its higher homologs are important phytotoxicants, even though they are present at concentrations of only a few percent of the total oxidants.

Jaffe (1967) reviewed published data on vegetative effects of PAN and other photochemical oxidants and summarized studies of both short- and long-term effects on several plant species. These summaries are shown in Tables IV-17 and IV-18.

Relative toxicity of PAN and its higher homologs indicated by fumigation of two plant species (Taylor, 1969) is shown in Table IV-19. Concentrations of the order of a few ppb are seen to result in injury at exposure times of 0.5 to 4 hours. These time-concentration conditions are similar to those observed in ambient atmospheres of smog-affected urban areas (Taylor, 1969).

3. General Symptoms of Pollution Injury to Vegetation

Assessment of the effects of pollution vegetation is generally based on characterization of injury symptoms. Brandt and Heck (1968) stated that symptoms of injury observed on the leaves of plants attributable to air pollution are: (1) leaf tissue collapse with necrotic patterns, (2) chlorosis or other color changes, and (3) growth alterations and/or suppression. In many cases, the injury pattern developed is highly characteristic of the toxic agent; however, the patterns may not always be specific. Disease, insects, nutrition and other factors can produce the same leaf patterns.

Table IV-17 - Typical Short-Term Effects on Photochemical Oxidants on Vegetation

Effects	Species	Pollutant	Concentration (ppm)	Length of Exposure
Leaf lesions (flecking) and tissue destruction (field studies)	Tobacco, Bel-W_3	Total oxidant	0.5-0.10 (avg)	2 hr
Leaf tissue destruction	Pinto beans	Total oxidant	0.11-0.15 oxidant maxima	24 hr (fresh plants exposed daily)
Leaf lesions and tissue destruction	Tobacco, Bel W_3	Ozone	0.5-0.10	2 hr
Leaf lesions and tissue destruction	Tobacco, Bel-W_3	Ozone	0.02	8 hr
Leaf lesions and tissue destruction	Petunia	PBN	0.005	7-8 hr
Leaf lesions and tissue destruction	Petunia Pinto beans	PAN	0.10	5 hr
Acute leaf tissue destruction	Pinto beans	Ozone	0.70	30 min
Acute leaf tissue destruction	Pinto beans	PAN	1.0	30 min
Inhibition of photosynthesis	Pinto beans	PAN	1.0	30 min
Changes in cellular chloroplast structure	Pinto beans	PAN	1.0	30 min

Table IV-18 - Typical Prolonged Effects of Photochemical Oxidants on Vegetation

Effects	Pollutant	Concentration (ppm)	Length of Exposure
Retardation of browth and reduction in yield			
Reduction in fresh wt (Tomato >22%)	PAN	0.005-0.015	5-6 hr/day, 5 days
Reduction in dry wt (Tomato >22%)	PAN	0.005-0.015	5-6 hr/day, 5 days
Reduction in fresh wt (Petunia >36%)	PAN	0.005-0.015	5-6 hr/day, 16 days
Reduction in dry wt (Petunia >28%)	PAN	0.005-0.015	5-6 hr/day, 16 days
Reduction in flowering (Petunia >41%)	Ozone	0.10-0.20	8 hr/day, 9 days
Reduction in stem elongation (Petunia >12%)	Ozone	0.10-0.20	8 hr/day, 9 days

Table IV-19 - Relative Phytotoxicity of PAN Homologs on Two Plant Species (a)

Fum. hr.	PAN(1) Conc. ppb	PAN(1) % Injury	PPN(2) Conc. ppb	PPN(2) % Injury	PBN(3) Conc. ppb	PBN(3) % Injury	Piso BN(4) Conc. ppb	Piso BN(4) % Injury
Bean (var. Pinto)								
0.5	---	---	100	90	100	80	100	80
1.0	140	55	24	7	30	59		
4.0	20	44	5	100				
Petunia (var. Rosy Morn)								
0.5	---	---	50	7	100	90	25	18
1.0	140	33	24	35	12	45		

(1) Peroxyacetyl

(2) Peroxypropionyl nitrate

(3) Peroxybutyryl nitrate

(4) Peroxyisobutyl nitrate

(a) Percent injury based on acute symptoms of tissue collapse.

General effects as described in The Air Quality Criteria for Hydrocarbons (1970) are: (1) acute, characterized by tissue collapse and necrosis of leaf parts, usually accompanied by a rapid change in leaf color; (2) chronic, identified by slow development of mild or severe symptoms over a long period, such as chlorosis without death of cells.

The terms "injury" and "damage" are often used interchangeably. As recommended by Guderian (1960), Heggestad (1968), Stern (1968) and in the handbook by Lacasse and Moroz (1969), plant damage indicates an economic loss and a change in the usability of the plant. Injury includes all responses of the plant to a pollutant, but such injury does not necessarily constitute a basis for economic loss.

Brandt and Heck (1968) gave an excellent summary of air pollutant injury patterns. Those pertinent to this study are given as follows:

a. Ethylene -

1) Leak markings

...Broad leaf - Epinasty and/or abscission of leaves without markings. Sensitive plants may develop general chlorosis of older leaves, necrosis, and leaf abscission. Stimulation of lateral development and finally death of plant may result. Abscission of young flower buds and/or failure of floral blooms to open. More resistant plants may show only retardation of growth and possible loss of apical dominance.

...Grasses - Retardation of growth with high suckering rate. No visual damage even at high concentrations.

...Conifers - Abscission of needles, retarded elongation of new needles, abscission of young cones or poor cone development.

2) Similar markings

...Broad leaf - Water stress (welting), bacterial wilts, root upsets, nematode and aphid injury,early senescence.

...Grasses - Suppressed growth and lack of markings are dissimilar to other disorders.

...Conifers - Water stress, other pollutants.

b. PAN -

1) Leaf markings - These are the following types:

...Broad leaf - On leafy-type vegetables and some other plants, a collapse of the tissue on the underside of the leaf giving a glazed, silvered, or bronzed appearance. On tobacco, petunia and similar leaves, collapse may be through the thickness of the leaf, usually in a banded pattern; on some, a blotchy pattern slightly resembling sulfur dioxide injury, but usually without the typical bleach. An early maturity or senescence is also associated with PAN.

...Grasses - Irregular collapsed banding bleached yellow to tan, sometimes appearing more as a chlorotic or bleached band than necrotic.

...Conifers - Not highly specific needle blight with some chlorosis or bleaching.

2) Similar markings -

...Broad leaf - "Sun scald", various virus and fungus diseases which produce blotchy pattern. Typical silvering is seldom duplicated by other agents.

...Grasses - Various fungal and bacterial blights produce streaked and banded markings.

4. Economic Crop Losses

It has been stated that plant damage is an important economic loss to farmers and an important esthetic loss to home owners. Although it is impossible to make a fire assessment of the cost of air pollution damage to vegetation, a recent estimate (Air/Water [1970]) indicates crop damage in California alone exceeds $100 million per year and reaches $500 million per year for the entire nation. It has been recently stated that air pollution damage to agriculture in California's two major smog areas totalled more than $44 million during 1969; these were conservative estimates. This latter report showed the citrus industry hardest hit, losing more than $33.5 million, with extensive damage also done to the following crops: grapes - $935,000; beans - $826,000; alfalfa - $500,000; celery - $367,000; tomatoes - $270,000; barley - $170,000; sweet corn - $163,000. Significant losses also affected apples, avocados, figs and pears; lighter damage was done to grass, hay, spinach, lettuce, radishes, turnips, endive, and rhubarb.

Values given for economic crop losses are only estimates, however, and other states are not as advanced as California in air pollution work. Only continued studies made nationwide will give reasonable numbers. It is very difficult to assess economic effects of plant damage caused by specific air pollutants. A number of factors and variables are involved in damage to vegetation. A partial listing includes damage related to moisture supply, chemical element supply, soil structure and atmosphere, temperature, toxic agents such as soil water pollutants and pesticides and damage by insects and pathogenic microorganisms. These damaging conditions and agents operate both below and above the soil surface. It is also apparent that various gaseous and particulate air pollutants, singly or in combination, damage vegetation. Synergistic effects of combined air pollutants, both organic and inorganic, have been noted, however, few specific studies have been reported.

Summaries of the factors involved in assessment of crop losses are given by Lacasse and Moroz (1969) and Stern (1968).

Hall (1957) described ethylene damage to cotton and other crops growing in the vicinity of an industrial ethylene plant located on the Gulf Coast of Texas. Measurements of atmospheric concentrations of ethylene ranged from 0.05 to 3 ppm. Cotton was found to be extremely sensitive whereas monocotyledonous crops such as sorghum and corn were relatively insensitive. Most of the vegetative symptoms observed were confined within a 2-mile radius; the most pronounced effects occurring downwind; increasing with nearness to the industrial site.

Downwind at a distance of 2000 feet, the growth of young plants was severely inhibited. Leaves fell from the plants, leaving bare stems. The leaves of older plants developed pronounced puckering and water-soaked appearing areas. Often the tissue developed a slight reddish color. At a distance of 0.8 mile and mostly downwind from the source, the plants showed a loss of apical dominance and developed a prostrate, vine-like habit of growth. The plants developed flower buds earlier and more profusely than normal, but most of these abscised while still quite small.

Similarly, the young fruits that did develop became prematurely detached. As a result, there was a complete loss of yield. At a distance from 1 to 3 miles, symptoms were greatly reduced, and only occasional slight effects were observed at a distance as great as 4 miles.

5. Summary

Ethylene has been shown to be the only important hydrocarbon causing injury to vegetation; aldehydes have not been proved to produce injurious effects on crops. The photochemical organic oxidant PAN appears to be a very important cause of plant injury and may be more widespread than thought.

Ethylene produces symptoms of plant injury which are not as recognizable as those produced by PAN; diagnosis of plant injury by air pollutants is thus a difficult task. Many environmental and pathological conditions produce plant injury symptoms which are difficult to differentiate from those caused by air pollutants.

CHAPTER IV

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B. HEALTH EFFECTS

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V. SYSTEMS MODEL

A. INTRODUCTION

This chapter describes the development of a systems model designed to quantitatively set forth the costs and benefits to society of hydrocarbon pollutant control systems. The model development was specifically oriented toward stationary source hydrocarbon emissions; however the model is general and can be adapted to other types of air pollutant emissions.

The lack of sufficient data to quantify the specific cost/benefit relationships resulted in a descriptive model useful primarily for the identification of existing data gaps and deficiencies to be filled by future R&D programs.

The specific goals of the modeling effort, expressed as desired outputs of the model, were:

- Definition of the socio-economic costs of hydrocarbon pollution

- Quantification of measures of control effectiveness

- Benefit/cost evaluation of control systems or control alternatives

- Enumeration of data deficiencies

The methodology of cost/benefit analysis of air pollution and the associated problem areas have been discussed by a number of authors, eg. Kneese and Wolozin (1966); Kneese (1967); Lave (1970); and Ridker (1967a).

The anticipated problems, common to regulatory benefit/cost analyses, included: the non-existence of a market for determination of the benefits of pollution reduction; the measurement of economic externalities; and the determination of realistic discount rates. Particular attention was paid to factors such as double counting, distributional effects, and discount rates, detailed later under assumptions.

Additionally, the review of adverse effects of hydrocarbon pollutants showed that specific input data was lacking to establish valid relationships between hydrocarbon pollutants and the adverse effects on society resulting from their emission. As discussed in detail in Chapter IV, documented human health effects of low ambient concentrations of hydrocarbon pollutants are limited to observations of eye and respiratory irritation from exposure to the low molecular weight aldehydes. The major adverse health effects derive from the secondary pollutants resulting from atmospheric photochemical reactions which involve not only hydrocarbons but other reactive atmospheric pollutants as well. Adverse effects on vegetation result almost solely from exposure to ethylene and the photochemical oxidants in smog.

The model examines damage caused by hydrocarbon emissions from stationary sources in five basic categories; damage to humans, animals, materials, vegetation and also indirect damage. To the extent possible within the limitations of the input data, eight functional relationships were developed for each of the five categories. These relationships are:

1. Socio-economic costs as a function of the adverse effects on the five affected categories (humans, animals, etc.).

2. Adverse effects as a function of ambient pollutant concentration and synergism.

3. Ambient pollutant concentration as a function of concentration in source effluent and of meteorological conditions.

4. Socio-economic costs as a function of point-source effluent concentrations, volume of emissions, and meteorological conditions.

5. Socio-economic costs as a function of multiple-source synergism.

6. Socio-economic benefits as a function of reduction of pollutant emissions.

7. Reduction of pollutant concentrations as a function of control systems costs.

8. Socio-economic benefit for reduction in concentration of a specific pollutant as a function of the control system cost.

By formulating these functional relationships for the affected categories and distributing them according to the distributions of the categories within the given demographic sector, one can compute the benefit-cost relationships for a given stationary source. By looking at the benefit-cost relationships as functional (distributional) values rather than purely specific (single-point) values, one can readily see the tradeoffs required to determine an optimal allocation of resources.

Although the necessary input data were lacking for the complete modeling of the cost/benefit relationships, the methodology is illustrated by two examples; human health effects of formaldehyde exposure and vegetation damage from ethylene exposure. The assumptions required in developing these examples limit their usefulness and they are presented solely for illustration.

B. MODEL DEVELOPMENT

This section describes the mathematical model that was developed to quantify the benefit-cost relationships of hydrocarbon pollutant emissions from stationary sources and corresponding control systems. The underlying concepts, background thoughts, and the general process related to the model's development are explained.

To decrease the chances of "double-counting" (i.e., including the same effect in more then one category) and to allow inclusion of all possible effects, the benefit-cost factors were assigned to one of five categories or adversely affected groups. These categories were chosen to be as orthogonal (disjoint and non-additive) as possible. The five categories encompass costs of damage to (1) humans, (2) materials, (3) animals, and (4) vegetation, and also include (5) indirect costs. Descriptions of these categories follow.

1. Human - Effects on humans are divided into two sub-categories; psychic and physical. The psychic sub-category includes the effects of odors, loss of visibility and the psychic aspects of physical damage to human

health as well as to the other adversely affected categories (materials, animals, etc.). Psychic effects and their associated costs cannot usually be expressed in quantitative terms and thus were recognized but not included in the model.

The physical sub-category includes: sensory irritations (eye, nose, throat, etc.); lost working time; morbidity (illness or health damage more severe than that causing lost working time); and mortality. There are two possible ways to estimate the cost of physical effects on humans: (a) to compute the actual medical costs and/or the lost time costs and use these as the cost to the person; and (b) to determine the amount a person would be willing to pay in order to avoid lost time and/or illness. The latter method probably provides the best estimate of the benefits that may be attained by reduction of human damages due to air pollution (Lave, 1970), but the data in the form of (a) above are much more readily obtainable (Rice, 1966; Ridker, 1967a; Kneese, 1966a). For reasons of availability only, the model development considered only actual costs of illness and/or lost working time.

Even partial damage to the health of a susceptible individual may affect work production (Rice, 1966) and thus loss in production may be an additional cost (and a possible benefit if the loss is eliminated). Again, of course, it is very difficult to separate the portion of production loss due to pollution from the portion that might have occurred even if the pollution were not present.

Multivariate statistical analysis techniques, implemented on some of today's large scale and very fast computers, may be one possible approach to the determination of loss of production due to pollution.

A relatively simple way of cost-evaluating physical damage to humans that results in mortality is to discount the wages of those who work. This method constitutes a drastic oversimplification, however, and of course provides no means of evaluating costs of non-workers. Much additional study is needed in this area (Sirageldin, 1969). If mortality is brought on by excessive pollution, the discounted cost of burial must also be considered.

2. Materials - The assessment of economic costs of materials damage by air pollution has been examined by Kneese (1966a), Lave (1970), and Ridker (1967a). Pertinent cost factors include the cost of increased maintenance (cleaning, painting, etc.), the cost of replacement of deteriorated materials (or depreciation costs if determinable), and reduced property values. Data on these cost factors are available, but the major difficulty lies in separating the effects attributable to specific pollutants from the total air pollution effects. Detailed study of isolated episodes has been made (e.g. chapter 5 of Ridker, 1967a), but further research is required to allow separation of the effects of hydrocarbon pollutants.

   Wohlers and Feldstein (1965) estimated the annual cost of damage to materials by photochemical smog products in the San Francisco Bay Area from limited data on the relative service lives of fabrics, plastics, and rubber products. Since the major damage resulted from ozone or total oxidants attack on these materials, it may be assumed that materials damage from hydrocarbon pollutants in nonsmog areas may be slight.

3. Animal - The animal category includes physical damage (morbidity and mortality costs), production losses, and psychic costs due to morbidity and mortality of pets. Physical damage includes the increased cost of maintenance of animals, e.g. supplemental feeding, cleaning, etc. Again, no data are available for separating those effects and related costs attributable to hydrocarbon pollutants.

4. Vegetation - The effects of hydrocarbon pollutants on vegetation may be assessed by treating the costs of replacement or increased maintenance of ornamental plants and the loss of production from commercial operations, such as commercial farming, cut-flower production, orchards, and forestry. Separation of the effects of specific pollutants on vegetation is more readily attainable than in the others

(human, materials, etc.), however, much of the vegetation damage results from exposure to photochemical smog products derived from not only stationary source hydrocarbon emissions but other sources as well.

Again, psychic costs that are not readily estimated may result from damage to ornamental plants and natural scenic areas.

5. Indirect Costs - This category was included in the model to handle economic effects not directly attributable to the other specific categories. Examples of indirect costs could include individual adjustments employed to compensate for or alleviate the direct effects of pollution (Ridker, 1967a), such as the cost of moving to a less polluted area or the cost of installation of air conditioning to minimize respiratory irritation. Considerable care must be taken in treating such indirect costs or adjustments to avoid double counting.

Given these five categories, the functional relationships outlined earlier were developed mathematically to provide a model suitable for quantitative evaluation of the socioeconomic benefit for a reduction in quantity of emissions as a function of the cost of control.

Before developing the mathematical relationships, certain important assumptions pertaining to the implementation of the general relationships were required. These assumptions are discussed in the following sub-section.

C. ASSUMPTIONS

The original concept for treating the economics of hydrocarbon pollution control was to develop a model that would relate the cost of control to the social and economic benefits resulting from control or reduction of emissions. Such a model was developed but because of a lack of input data it could not be adequately implemented. To demonstrate the use of the model, various assumptions were made. This section enumerates the important assumptions and discusses the reasons for choosing one direction or specific value over other alternatives. These assumptions relate to property values; chronic vs. episodic exposures; derivative effects; distributive effects; discount rates; meteorology; geographic and demographic distribution; control effectiveness; and recent prices.

Property Values - An important assumption was that property values cannot be used as a direct measure of the effects of hydrocarbon air pollution, primarily because of the difficulty of separating the effects of hydrocarbon pollution from other factors affecting property values.

Another reason for not using property values is that the most readily available data, that of assessed property values, does not correlate well with real property values (Davis, 1969).

Chronic Versus Episodic Exposures - Although much more investigation of the chronic toxicity of hydrocarbons remains to be done, the literature data indicate that no serious chronic health effects result from exposure to average ambient air hydrocarbon concentration. It has been assumed, therefore, that health effects of hydrocarbons are primarily related to acute or episodic exposure to higher than average ambient concentrations.

Even for localized areas near a continuous point source emission there will generally be daily fluctuation in wind directions and velocities that provide periods of sufficiently low concentration to allow recovery (assuming no physiological build-up). Thus, health effects may be estimated, at least for illustrative purposes, on the documentation used for developing Threshold Limit Values (TLV) (American Conference of Governmental Industrial Hygienists, 1971).

Derivative Effects - The effects of hydrocarbon pollutants may be minor in certain areas compared with the effects of the hydrocarbon derivatives, such as photochemical smog. The probability of smog formation in a given area depends critically on the topography and meteorological conditions present, in addition to the types and amounts of hydrocarbon emitted from both stationary and mobile sources. The difficulties in atmospheric diffusion modeling of smog reactions and the lack of data for adequate separation of stationary and mobile source smog contributions effectively prevented consideration of derivative effects. For the illustrative examples, we arbitrarily assumed that no photochemical smog was involved.

Distribution Effects - Distribution effects (i.e., the relocation and/or reallocation of people and/or resources) were arbitrarily assumed to be negligible. This assumption should be given careful consideration in future studies. Changes in pollution levels brought about by applied controls will probably result in significant reallocation of labor resources and consumer dollars to other parts of the economy. These distribution effects will be more pronounced for those people in industries directly dependent on the effects of pollution (e.g., service industries) than for the general populace.

Discount Rate - Before making any assumptions about discount rates, several discount rates were examined to determine the effects on long-range items such as mortality, future burial costs, etc. (for burial costs see Ridker 1967a and Kneese 1966). For this model it was arbitrarily assumed that a long-term discount rate of 6 percent was representative (Rice, 1966). A higher discount rate would decrease the present value of future costs or benefits and a lower rate, which discounts future expenditures by a smaller compounded amount, would increase the present values. The discount rate does not have a significant effect in the short term (2 to 3 years).

Meteorology - Although the model is designed to allow inclusion of various meteorological distributions for difficult regions of the country, simplifying assumptions were made in the illustrative examples. It was assumed that meteorological conditions for exposed people and materials were linearly ordered. For the estimation of downwind pollutant concentrations, the graphical approximations given by Turner (1970, revised) were used, assuming average low wind velocity and atmospheric stability class (slightly unstable). Estimates of downwind concentrations for a number of point source types showed that the principal effect of different wind velocities and stability classes was to change the downwind distance at which maximum concentration is attained, with little effect on the maximum concentration (for effective stack heights of 100 meters or less).

Geography and Demography - Both geography and demography are important factors in evaluation of air pollution effects. Geography is important because of the different meteorological conditions in differing types of terrain and of land-use. Demography is important because factors such as age, income, and susceptibility to disease have definite effects on the human costs of air pollution. The model allows geographical or regional effects to be adjusted for human regional differences as well as meteorological differences.

For ease of calculation, the examples assume that the human damage figures are for a person who lives in an urban air basin, of average health, age 25 to 29, earns average income for his age, makes no leisure time economic contribution, and has linearly ordered pollutant damage. Distributions for almost all of these factors are available in published statistical compilations and can be put into the model as desired.

Control Effectiveness - The example calculations are based on the assumption of essentially complete removal of the pollutants under consideration.

Recent Prices - In application of the cost-benefit model, prices should be reviewed, and, where warranted, updated. For example, the average income of 25 to 29 year old males may change as may the recent cash price of 26¢/lb for cotton.

D. MATHEMATICAL MODEL

This section describes the model in terms of the mathematical relationships required for implementation. Before describing the functional relationships, we define the notation in which these relationships are expressed. Definitions are given in four groups:

1. Lower Case - Primarily sub or super scripts

Letter	Range	Description
a	a = 1 to 85	a specific age
b	b = 1 to h	a human disease type
c	c = 1 to p	a type of crop or vegetation
d	--	a death
e	--	a burial
f	--	indicates a function
g	--	indicates a function
h	*	the limit of human fisease types
i	i = 1 to n	a specific pollutant
j	j = 1 to 5	a category that can be affected by a pollutant
k	k = 1 to m	a specific region of the country
l	*	the limit of the control systems
m	*	the limit of the regions
n	*	the limit of the pollutants
o	--	normal replacement
p	*	the limit of the vegetation
q	*	the limit of the acreage
r	--	a counter used in discounting to present value
s	s = 1 to q	area of affected crop (acres)
t	t = 1 to l	a specific control system
u	--	indicates a function
v	*	the limit of units of washing, cleaning or maintenance
w	w = 1 to v	a unit of washing, cleaning or maintenance
x	--	earlier than normal replacement
y	y = 1 to z	a specific material
z	*	the limit of materials

Symbol		
'	--	indicates application of control
ψ	--	to indicate a function
γ	--	the interest rate

* depends on available data
-- range is not applicable

2. Upper Case - Major notation

Letter	Description
A	ambient concentration
B	total benefit
C	component cost
D	adverse affect
E	an expected value
F	change in pollutant's concentration
M	meteorological condition
N	distribution of types (e.g.b's within various categories
P	a probability or proportion
Q	quantity of pollutant in effluent stream
R	benefit/cost ratio
S	cost of control system
T	total cost
V	present value of future costs or benefits
Y	yearly or annualized number occuring

3. Major complete terms

Term	Description
D_{ijk}	variable specifying adverse affects of pollutant i on category j (where the affected categories are as originally specified - human, vegetation, etc.) and k is the region being considered.
A_i	ambient concentration of pollutant i
M_k	meteorological conditions for a given region, k
Q_i	quantity of pollutant i in effluent
S_{itk}	cost of control system, t, for pollutant i in region k
C_{ik}	socio-economic cost of hydrocarbon pollution for region k
N_{jk}	distribution of different types within category j in the region k
F_{itk}	reduction in concentration of pollutant i in region k by control system t
T_{it}	total cost of controlling stationary source hydrocarbon pollutant i with control device t
B_{it}	total benefit of stationary source pollution control of pollutant i with control device t

4. Benefit/Cost Functional Relationships

Working backwards, the mathematical functional relationships are specified for determining the benefit/cost ratio for reducing the concentration of pollutant i with control system t, summed over j categories and k regions.

$$(1) \quad T_{it} = \sum_{j=1}^{5} \sum_{k=1}^{m} S_{itjk}$$

$$(2) \quad B_{it} = \sum_{k=1}^{m} (C_k - C'_k)$$

$$(3) \quad C_{ik} = f_k (D_{ijk}),$$

$$\text{where } f_k = \sum_{j=1}^{m} D_{ijk}$$

$$\text{and } C'_k = f'_k (D'_{ijk}, S_{itk})$$

$$(4) \quad D_{ijk} = g(A_{ik}, N_{jk})$$

$$(4') \quad D'_{ijk} = g'(A'_{ik}, N_{jk})$$

$$(5) \quad A_i = \psi(M_k, Q_i)$$

$$(6) \quad F_{itk} = u(S_{itk})$$

$$(7) \quad A'_i = \psi'(M_k, Q_i, F_{itk})$$

Combining these relationships yields R, the benefit/cost ratio.

$$(8) \quad R_{it} = \frac{B_{it}}{T_{it}}$$

The benefit/cost ratio for all hydrocarbons is then derived from a matrix analysis of the R_{it} values.

The calculation of D_{ijk} across the affected categories is straightforward and should present no significant problems when the distribution of the types of effects are available for each category. Examples of several of the affected categories are described.

Human - Let j = 1 represent the human damage category. Then, putting aside regional (k) and control (t) distinctions for the moment,

$$D_1 = \sum_{i=1}^{n} f\text{ (medical costs)} + \sum_{i=1}^{n} f\text{ (mortality costs)} + \sum_{i=1}^{n} f\text{ (psychic costs)}.$$

As stated previously the examples used later assume f(psychic costs) = 0.

The medical cost of function is expressed as:

$$f\text{(medical costs)} = \sum_{b=1}^{h} P_{ib}\, C_b\, E\,(Y_b).$$

P_{ib} is the proportion of disease b caused by pollutant i, and is itself a function of ambient pollutant concentration, the types of people that may be affected, the quantity of pollutant in the effluent, meteorological conditions, and changes in concentration due to control action (Lave, 1971; Ridker, 1967a; Kneese, 1966a). C_b is the average annual cost per case of disease b (see disease types below) and $E(Y_b)$ is the total annual number of b diseases. The principal disease types include but are not limited to the respiratory diseases; cancer of the respiratory system, pneumonia, chronic bronchitis, acute bronchitis, emphysema, and asthma.

The mortality cost function is expressed as:

$$f\text{(mortality costs)} = \sum_{a=1}^{85} P_{ida}\, C_{da}\, E(Y_{da}).$$

P_{ida} is the proportion of deaths (d) caused by pollutant i at age a and is otherwise similar to P_{ib} in the preceding formula. C_{da} is the cost of death at age a and $E(Y_{da})$ is the expected number of annual deaths. Further, D_{da} is the present value of future earnings (V_{da}) plus the present value of the expected cost of burial (V_{ea}).

V_{da}, the present value of future earnings, at age a, is defined by the following expression (Rice, 1966):

$$V_{da} = \sum_{r=a}^{85} \frac{X_r W_r P_a{}^r}{(1+\gamma)^{r-a}},$$

where X_r is the annual mean earnings at age r; W_r is the single year labor force participation rate (ie, proportion of males, or females, of age r employed in any single year); $P_a{}^{\gamma}$ is the incremental probability that a male of age a survives to age r; and γ is the interest or discount rate.

When X_r is available only for age groups, the preceding expression can be readily modified, as was done by Rice (1966). This formulation assumed the use of male earnings only; it would be better to use full family incomes (Sirageldin, 1969) in this expression, but some of the required parameters are difficult to measure and would be expensive to obtain.

V_{ea} is the cost of burial discounted to the present by subtracting the net gain from delaying burial at age a. It is calculated (Ridker, 1967a) as:

$$V_{ea} = C_e[1 - \sum_{r=a} \{ \frac{P_a{}^{\gamma}}{(1+\gamma)^{r-a}} \}]$$

where C_e is the cost of burial and other terms are as previously defined.

Animal - Let j = 2 represent the animal damage category. Domestic productive animals can be equated to humans when their net productive contribution is considered as a "wage" using the formula for evaluating pollution effects on humans, with perhaps some rendering benefit and no burial cost.

Vegetation - Let j=3 represent the vegetation damage category. Then, again putting aside regional and control distinctions,

$$D_3 = \sum_{i=1}^{n} f(\text{crop damage}) + \sum_{r=1}^{n} f(\text{permanent soil damage}.$$

Assuming no permanent soil damage from hydrocarbon pollutants, the crop value, D_{i3}, is then the percentage of crop damaged and the area of the crop or:

$$f(\text{crop damage}) = \sum_{c=1}^{p} \sum_{a=1}^{q} P_{ics} C_{cs} E(Y_{cs}),$$

where P_{ics} is the percent damage due to pollutant, i, on a crop c, over s(acres) area, C_{cs} is the cost (or value of crop per acre) and $E(Y_{cs})$ is the expected annual acres of crop c. The discounted future cost of damaged crops could be included if the pollutant causes any lasting soil damage, but this discounting is not included in the present treatment.

Material - Let j=4 represent the material damage category. The, D_4=f(increased cleaning and maintenance) + f(earlier than normal replacement), or

$$D_4 = C_w + V_{x-o}.$$

C_w, the cost of extra washing, cleaning, or maintennace, is expressed as:

$$C_w = \sum_{i=1}^{n} \sum_{w=1}^{v} \sum_{y=1}^{z} P_{iwy} C_{wy} E(Y_{wy}), \text{ where } P_{iwy} \text{ is}$$

the percentage of washing or cleaning of material due to pollutant i; C_{wy} is the average cost of cleaning material y, and $E(Y_{wy})$ is the expected annual units of cleaning or washing material y.

The present value of earlier than usual replacement, V_{x-o}, is equal to

$$V_{x-o} = \sum_{i=1}^{n} \sum_{y=1}^{z} \left[\frac{E(C_{iyx})}{(1+\gamma)^r} \quad \frac{E(C_{iyo})}{(1+\gamma)^r}\right],$$

where $E(C_{iyx})$ is the expected cost of early replacement of material y due to pollutant i, $E(C_{iyo})$ is the expected cost of replacement of material y with the reduced exposure of controlled pollutant i, and γ is the years to replacement.

Indirect Costs - No indirect costs were included in these examples. Procedures for calculating indirect costs would be similar to those outlined above.

Some information was obtained on all of the preceding variables and functions, but little, if any, was available on the ranges or distributions of the variable values. Viable values for the benefit/cost ratios will require more information on all of the variables than is presently available. The preliminary examples shown in the next section were completed by assuming specific values for:

N_{jk} - The distribution of different types of effects within each of the j categories.

Q_i - The quantity of pollutant i in the effluent.

M_k - The meteorological conditions.

$u(S_{itk})$ - The function of the cost of control system t for pollutant i.

Values for all of these distributions affect the distribution of D_{ijk} and thus directly influence the calculations given in the following examples for formaldehyde and ethylene.

E. EXAMPLES

In the examples that follow, additional assumptions were required due to lack of explicit input data. These assumptions are explained as they occur.

1. Formaldehyde

Formaldehyde was selected as an example pollutant because it is one of the few hydrocarbon pollutants for which there are some data on human health effects resulting from exposure to low or moderate concentrations such as might be attained locally near a point source emission. Since much of the available data on formaldehyde effects are based on short term exposure (see Chapter 4 and also Community Air Quality Guides, "Aldehydes", 1968), the basis for estimating damage effects and costs was an 8 hour exposure period rather than continuous exposure.

By assuming a linear relationship between human health effects and formaldehyde concentration for an 8 hour exposure, the limited data on health effects versus exposure were used to develop the approximate relationship shown in Figure V-1. The extremes of the human effects scale used in Figure V-1 may be suspect, since Schuck et al (1960) reported mild eye irritation from exposure to concentrations in the range from 0.01 to 0.5 ppm. Additionally, there are no data on mortality resulting from chronic exposure.

Based on the assumptions described previously in Section C, the relationship between annual cost per person affected and the relative human health effects was estimated as shown in Figure V-2. It should be obvious from these assumptions that many of the important items (age, income, environment, physical condition, etc.) have wide and disparate distributions over the total population. Without adequate data on these distributions, computing the total effects, even of formaldehyde on human health, is functionally impossible and figures based on estimates or averages are practically meaningless.

Figure V-2 shows that the cost to society of human death is less than that of complete invalidism. As stated previously, the choice of a discount rate higher than 6 percent would lower the peak; a lower rate would make the peak higher.*

By combining the relationships shown in Figures V-1 and V-2, the annual cost per person affected as a function of formaldehyde exposure is obtained. This is shown in Figure V-3.

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* As calculated by the use of the expression for the present value of future earnings (p 15), the cost of mortality for the individual male, age 25-29, at a discount rate of 6 percent is $100,011 (Figure V-2), at a 4 percent discount rate the cost would increase to $128,698. The cost of complete invalidism is equivalent to the mortality cost plus the cost of health care service over the remaining life expectancy.

Figure V-1 Human Health Effects From Formaldehyde Exposure

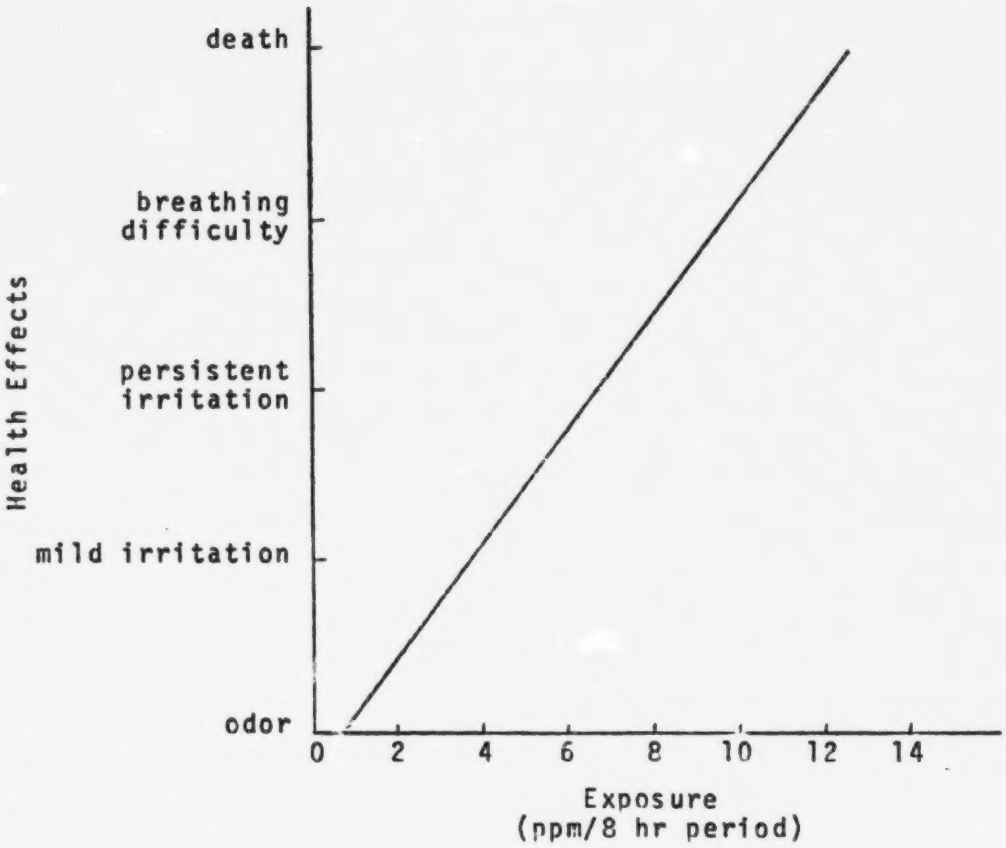


Figure V-2 Annual Per Person Cost of Formaldehyde Health Effects

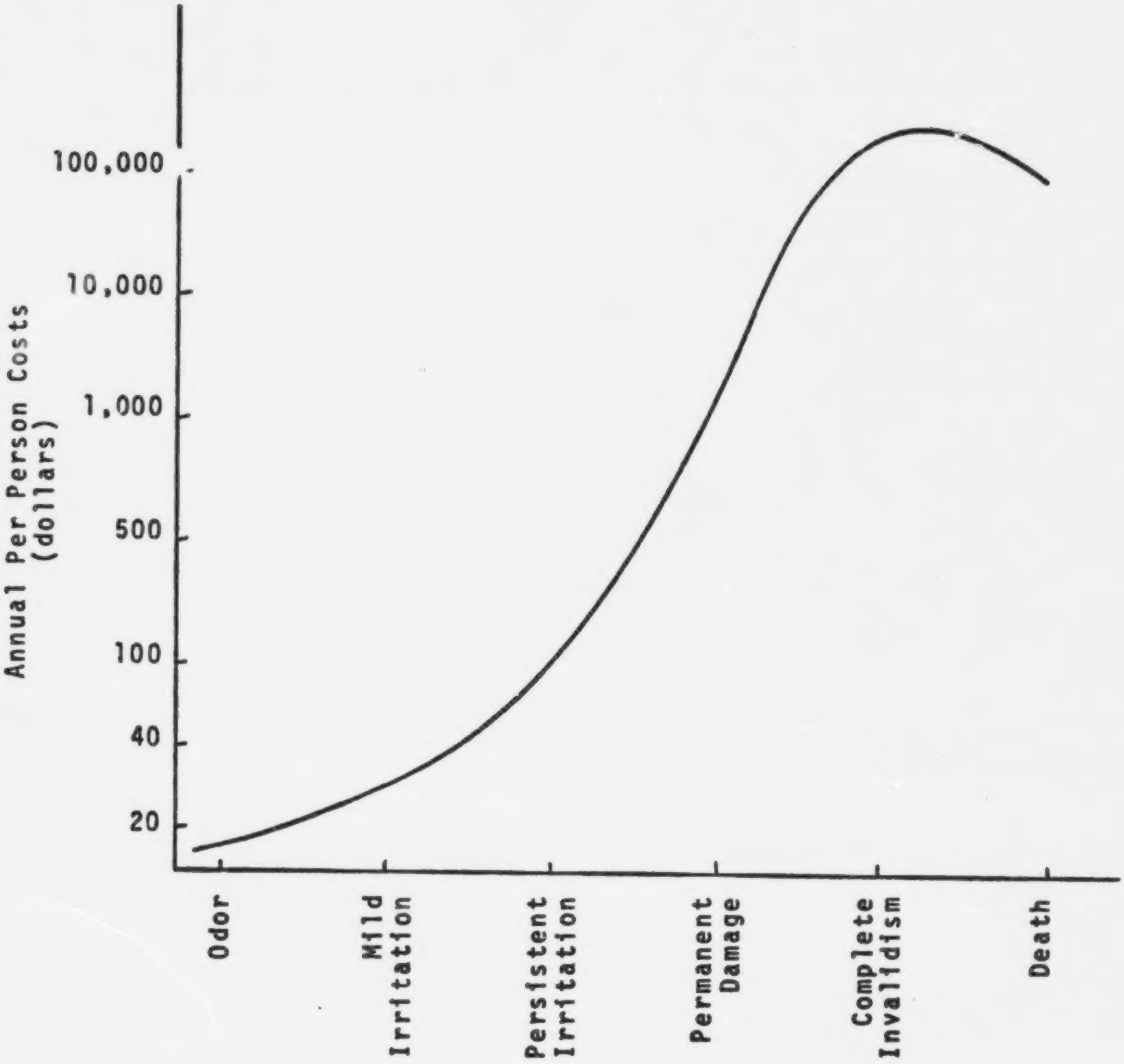
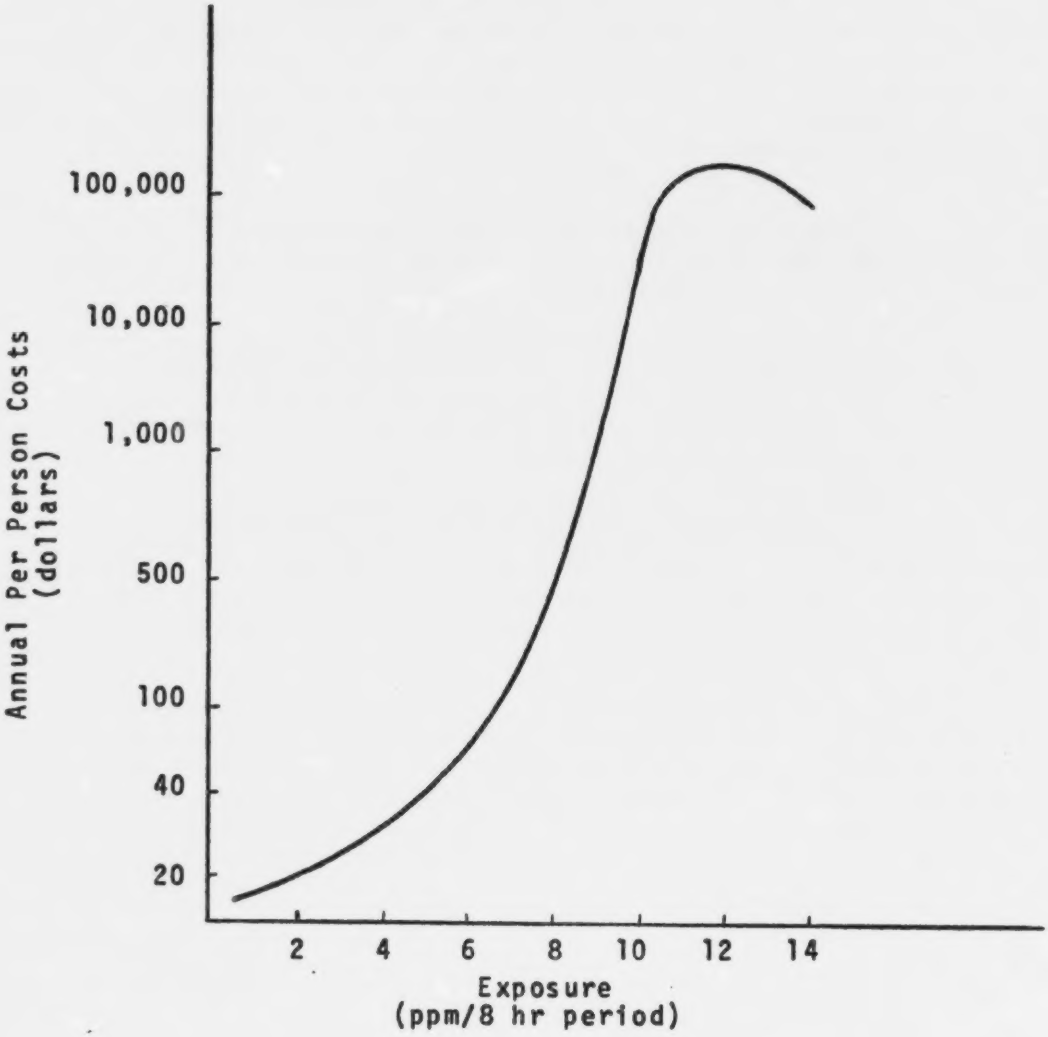


Figure V-3 Annual Per Person Cost as a Function of Formaldehyde Exposure



To complete this example, costs of formaldehyde emission control must be estimated. For simplification, a point source emission affecting an urban region of moderately level topography was chosen. The point source was a formaldehyde production plant producing 100 million pounds per year of 37% formaldehyde by methanol oxidation. Absorber vent gases (40,000 SCF/1,000 lb product) were assumed to contain 0.3 percent formaldehyde before control, or about 125 lb/hr formaldehyde emissions. For an effective stack height of 20 meters or less, maximum downwind concentrations would range from about 0.3 to nearly 20 ppm, depending on wind velocities and atmospheric stability (Turner, 1970 revised). At low wind velocities and moderately unstable atmospheric conditions, downwind concentrations would average about 4 ppm.

The cost of essentially complete control of these emissions by direct flame incineration was estimated to be $3.75/hour,* or $30,000/yr.

Figure V-3 shows that the estimated annual cost of human health damage from 4 ppm formaldehyde is about $25 per person. Assuming this concentration is constant, the costs and benefits as a function of the total affected population is shown in Figure V-4.

The equation for the benefit (damage) line is $y_b = 0.025x$ and the control cost line is $y_c = 30$. The benefit-cost ratio is therefore $R = Y_b/Y_c$ or $0.025x/30$. Putting this into a single graphical expression yields Figure V-5, in which the ratio line is described by $Y_r = 0.000833x$ or in terms of thousands of people, $Y_r = 0.833x$.

This latter figure (Figure V-5) shows that the expected annual benefits exceed the control costs when the population of the exposed area exceeds 1,200 people. The assumption that all persons in the affected area receive the same exposure is significant, since actual concentrations in any air basis vary considerably; realistic estimates of the concentration distribution would require the output of a sophisticated atmospheric diffusion model.

* Estimated from natural gas fuel costs ($0.60/$10^6$ BTU) of $3.25/hr plus fixed costs of $0.50/hr for incineration with no heat recovery.

Figure V-4 Annual Human Benefit-Cost for Formaldehyde Emissions Control

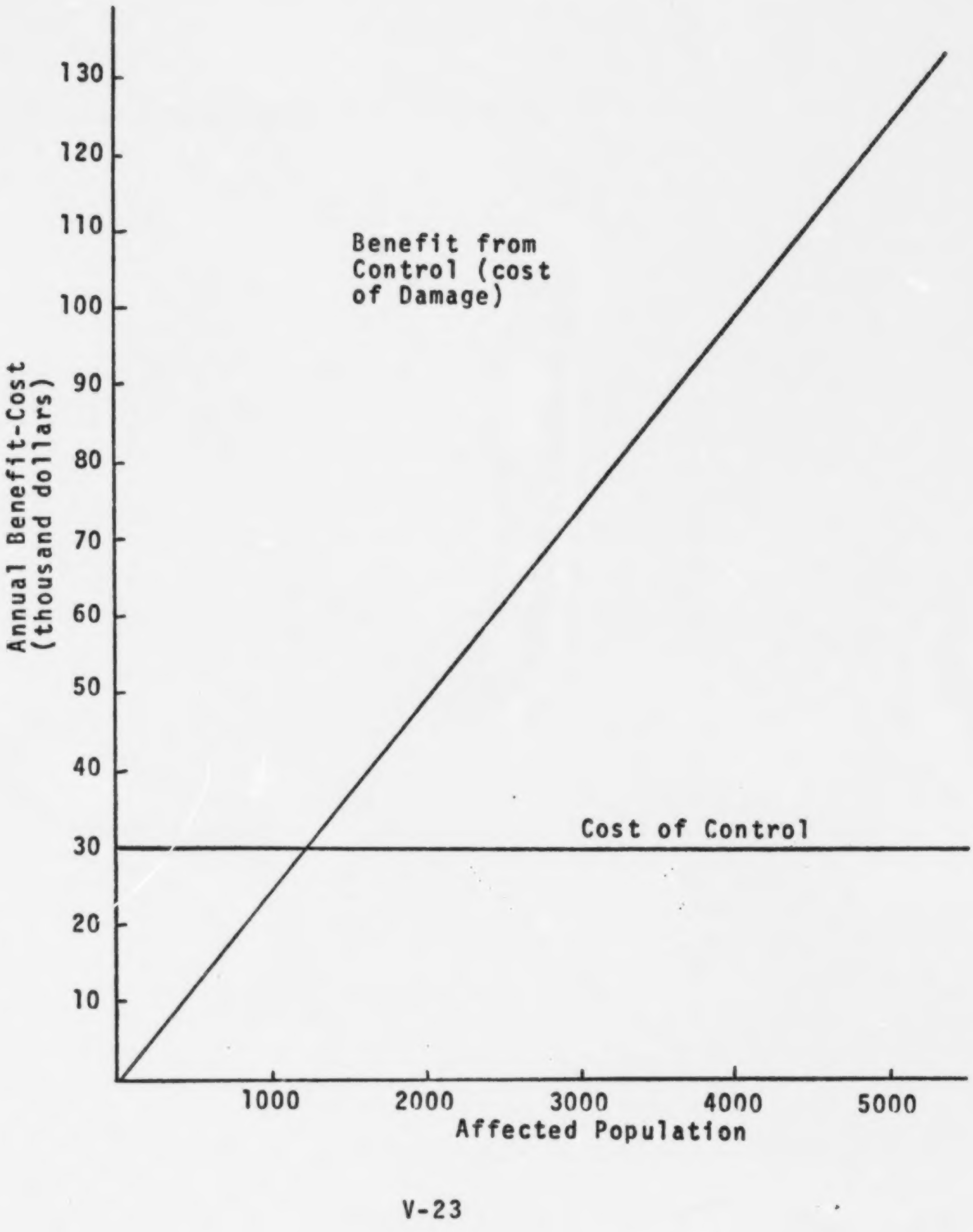
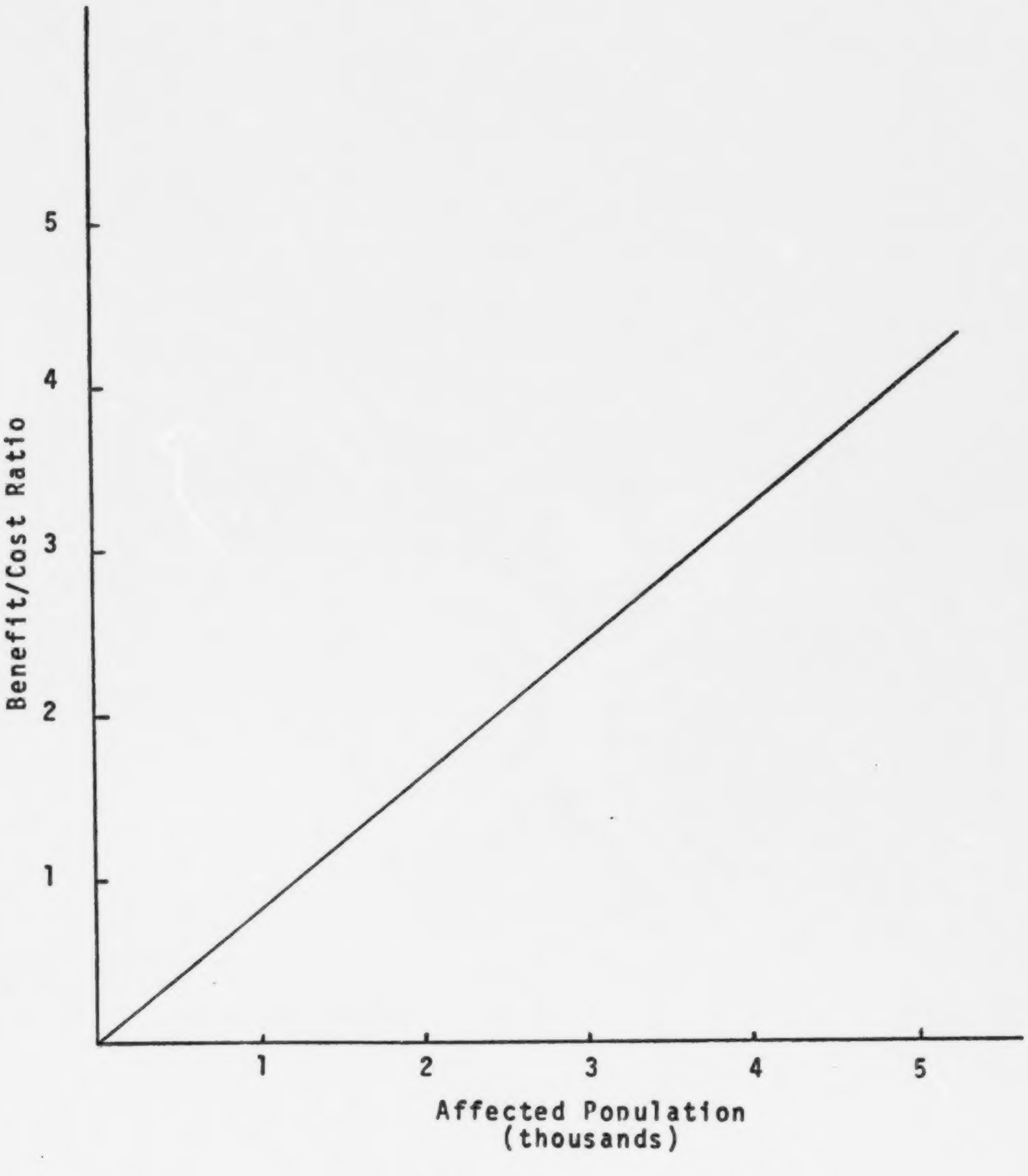


Figure V-5 Benefit-Cost Ratio for Formaldehyde Control



2. Ethylene

The previous example treated a hydrocarbon pollutant that has primarily human health effects (formaldehyde has not been shown to have demonstrable adverse effects on vegetation or materials). For the second example, ethylene was selected as a pollutant having primarily vegetation damage effects. Human health effects of ethylene are limited to primarily asphyxiant effects at fairly high concentrations (TLV=1000 ppm). Other human health effects are those related to photochemical smog. Although ethylene is one of the known smog precursors, this aspect of ethylene damage was not considered in the example because of the difficulties, cited earlier, of evaluating health aspects of smog components.

Ethylene damage to vegetation, as detailed in Chapter IV, results primarily from growth inhibition and premature ripening of fruit.

Hall et al (1957) described the effects of ethylene emissions on a cotton crop so severe that the plants died within 2000 feet of the maximum downwind ground concentration. The effects of ethylene on vegetation are exemplified in Figure V-6, based on Hall's data for damage to cotton and other data given in Chapter IV.

Treating Hall's example of cotton damage, the vegetation damage from ethylene exposure can be expressed as the loss of cotton production shown in Figure V-7. Assumptions employed were an average cotton yield per acre of one net bale (∿480 lb) and a recent cash price of $0.26 per pound. Thus, the per acre cost of complete crop destruction would be 480 lb/acre multiplied by $0.26/lb or $124.80 per acre.

To complete the example, a point source of ethylene emissions was assumed to be a petrochemical plant producing 200 million pounds per year of polyethylene. Ethylene emissions were estimated at 450 lb/hr; this results in downwind concentration estimates (Turner, 1970 revised) in general agreement with those reported by Hall (1957), in the range from 5 to 10 ppm.

The cost of essentially complete control of the ethylene emissions by catalytic incineration was estimated to be $1.75/hr (Estimated from data in Appendix B for catalytic incineration with no heat recovery).

Figure V-6 Ethylene Damage to Vegetation

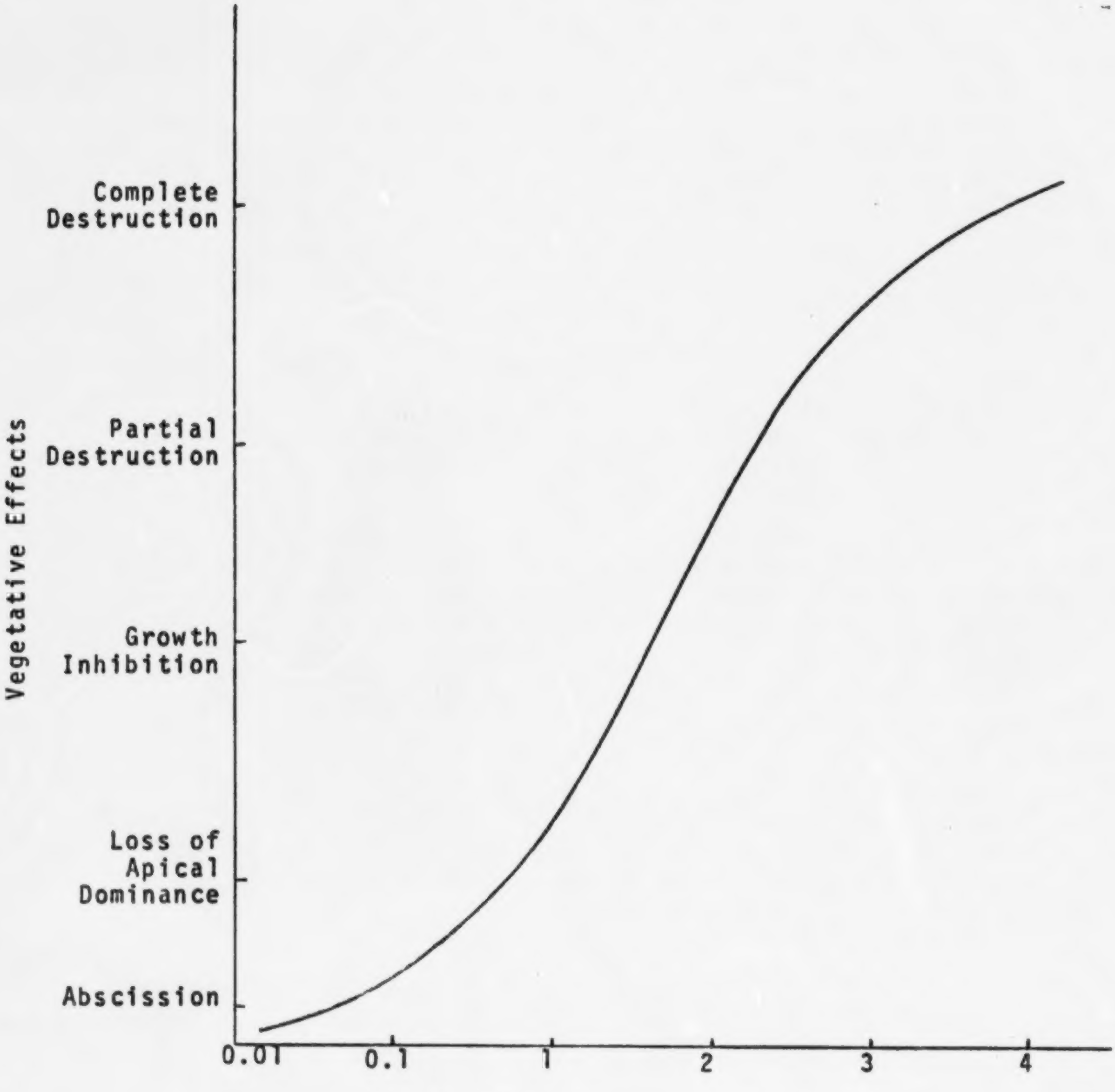
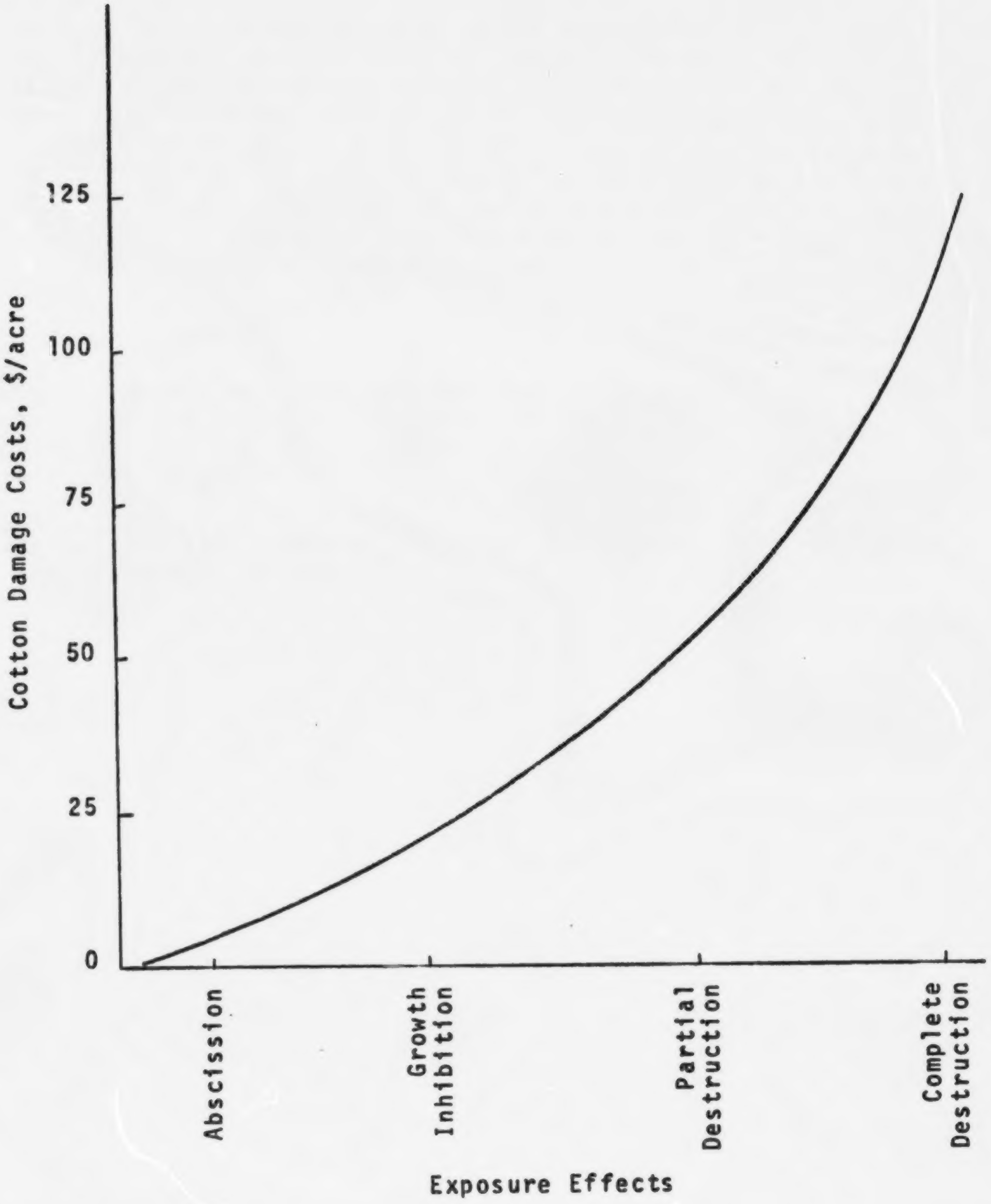


Figure V-7 Per Acre Cost of Ethylene Damage to Cotton



Combining the relationships given in Figure V-6 and V-7 yields the economic costs of cotton damage as a function of ethylene exposure, shown in Figure V-8.

Assuming an average uncontrolled downwind concentration of 5 ppm ethylene and the cost of control given above, the annual benefits (damage costs) and control costs as a function of exposed cotton acreage are shown in Figure V-9. Calculation of the benefit-cost ratio for ethylene control results in the benefit-cost ratio function shown in Figure V-10. This shows that control costs are exceeded by benefits when the exposed acreage exceeds 115 acres of cotton. The input data and assumptions do not warrant this degree of precision and do not take into account the concentration distribution.

F. DISCUSSION

The preceding examples required considerable oversimplification and extensive assumptions in order to illustrate the application of the benefit-cost model. It must be emphasized that these examples were purely illustrative and that considerable effort must be expended to provide the input data that would allow more meaningful modeling. For further testing, development, and eventual validation of the systems model, additional data are required. The more important missing input values are: D_{ijk}, f_k; $u(S_{itk})$; M_k; Q_i, $\Psi(M_k, Q_i)$; and N_{jk}.

Figure V-8 Per Acre Cotton Damage as a Function of Ethylene Exposure

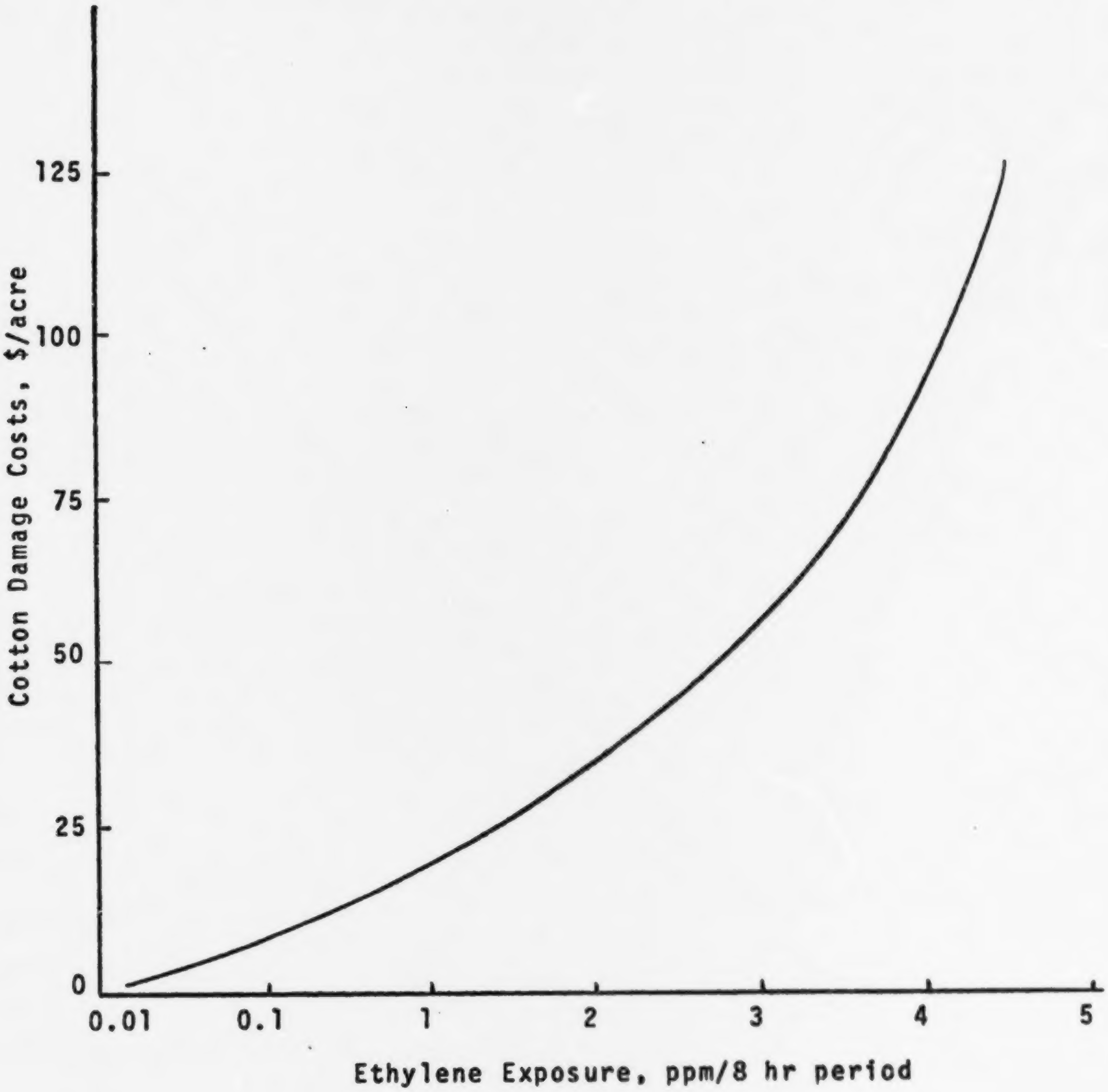


Figure V-9 Annual Benefit-Cost for Ethylene Emissions Control

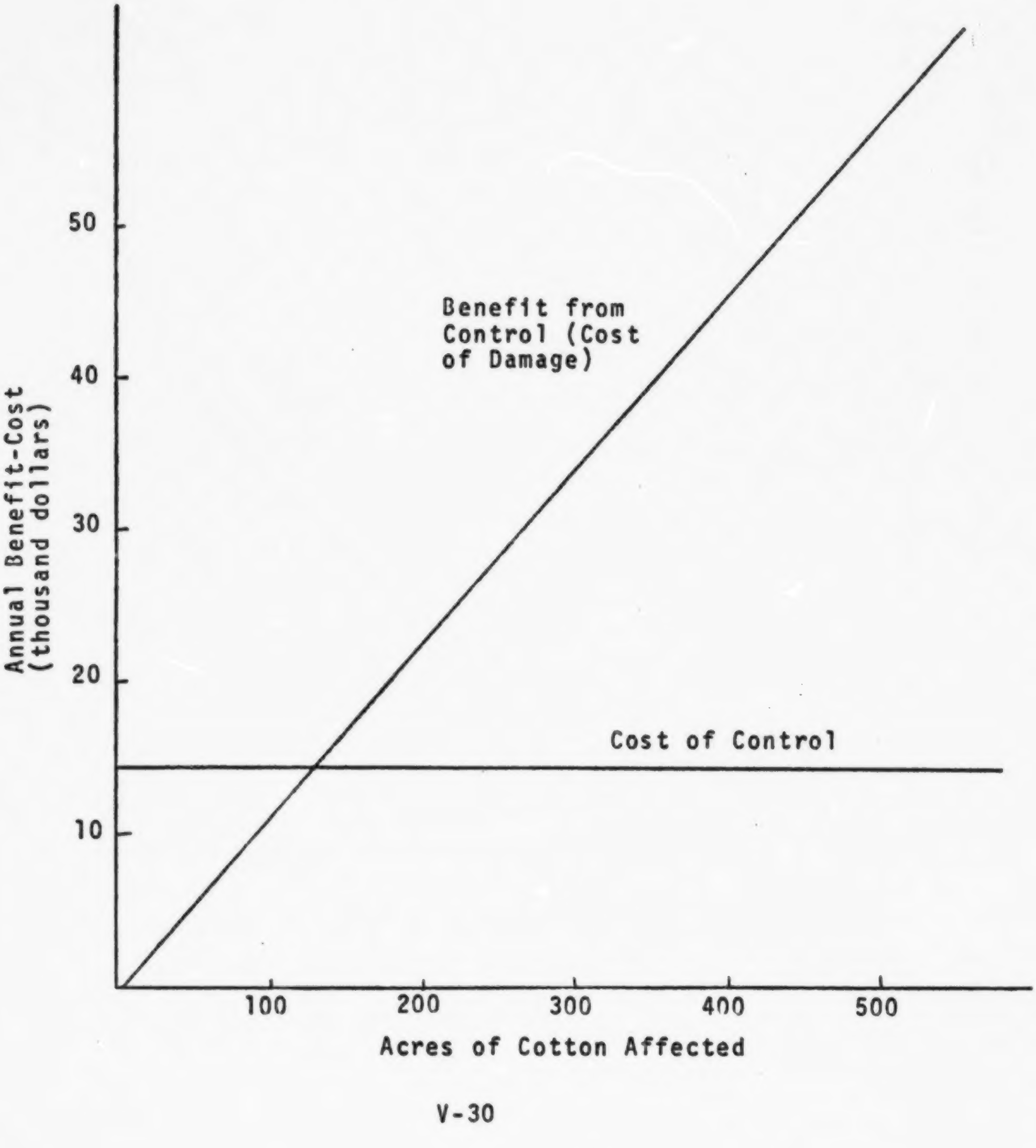
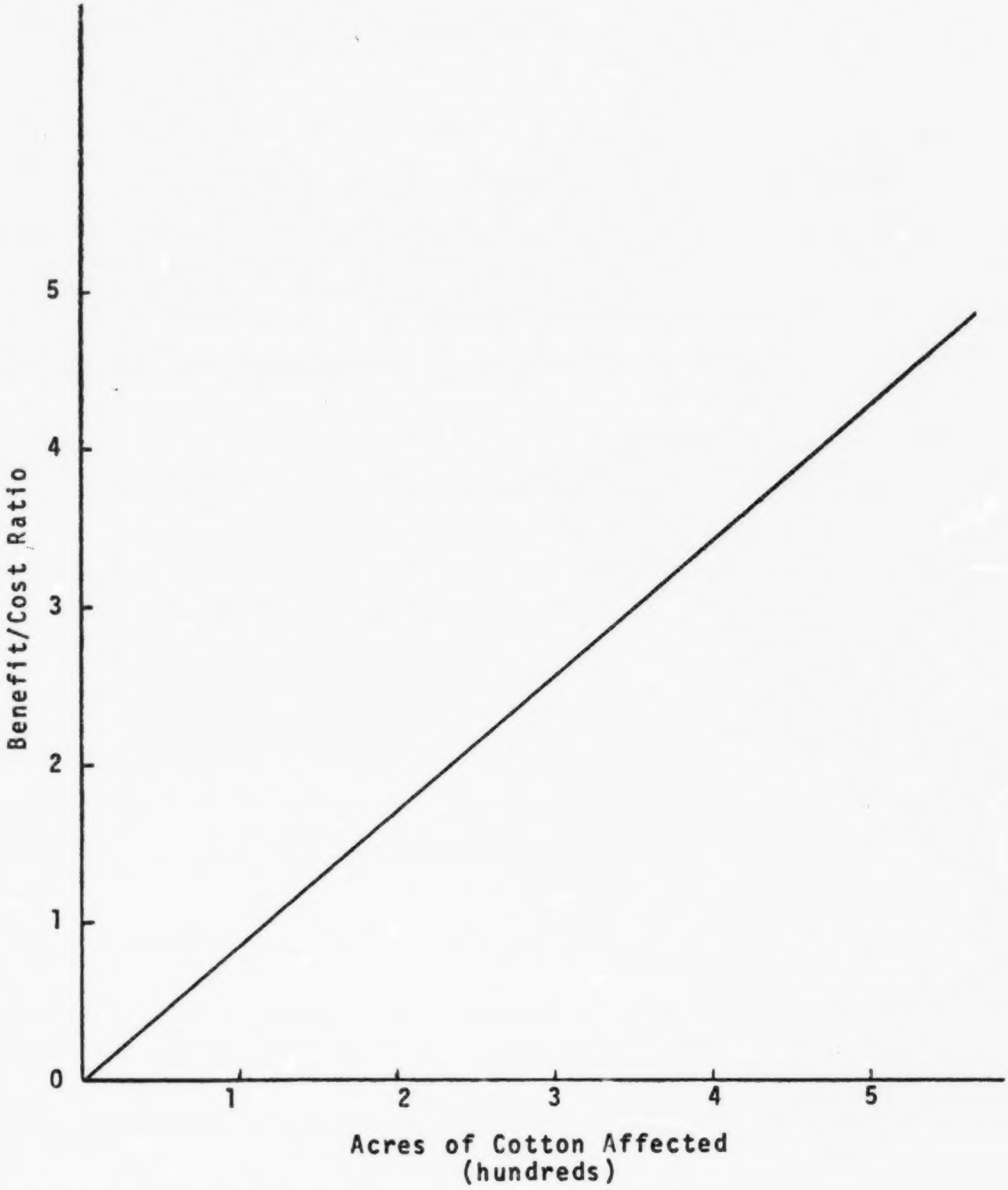


Figure V-10 Benefit-Cost Ratio for Ethylene Control



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VI. CONTROL OF HYDROCARBON POLLUTANTS

A. INTRODUCTION

The purpose of this phase of the study was to identify and evaluate engineering technqiues for the control of hydrocarbon emissions from stationary sources, with the ultimate objective of presenting a coordinated R&D planning program. To aid in establishing priorities and properly channelling future efforts, particular emphasis was placed on the identification of gaps in existing technology and design bases and the formulation of remedial experimental programs.

A review of the literature relating to hydrocarbon emission control was conducted to (1) assess the disadvantages and deficiencies in existing technology and (2) identify those control techniques for which general case economic evaluations would be of value.

This review of the open literature showed that, aside from the compilation of design procedures and case histories presented in the Air Pollution Engineering Manual (Danielson, 1967), there is very little in the way of published quantitative information on industrial application of hydrocarbon control processes and equipment. A review of hydrocarbon control technology was presented in Control Techniques for Hydrocarbons and Organic Solvent Emissions from Stationary Sources (U.S. Department of Health, Education and Welfare, 1970), but the treatment was largely qualitative and descriptive.

Much of the detailed information on the engineering design and application of control techniques resides in the files of engineering and equipment firms specializing in particular types of pollution control. Discussions with several such firms resulted in the release of hitherto proprietary information on design and application procedures. Some of this information is presented in the detailed engineering and economic studies in Appendices A through E.

Technology for the control of hydrocarbon emissions has developed rather unevenly. Primarily through the impetus of smog control programs in Southern California, the control and abatement of petroleum products and organic solvents by incineration or afterburning and carbon adsorption has been developed into rather straightforward procedures of engineering design and application. Other techniques, particularly wet scrubbing for absorption, direct-contact condensation, and wet particulate removal, lack a suitable design base.

Our review and ranking of organic pollutants and their effects showed that identifiable and proven adverse effects of organic vapors or gaseous emissions were limited to their contribution to photochemical smog and certain relatively minor health effects. This lack of documented adverse effects undoubtedly accounts for the unevenly developed state-of-the-art with smog control and nuisance abatement being strongly emphasized. In spite of the concern in some quarters over the status of the polycyclic aromatic hydrocarbons as potential carcinogenic agents, very little development of control technology for sources of these PAH's has been reported.

The control technologies that are the most advanced both theoretically and practically, are those used in applications offering a clear-cut economic advantage, either as prevented losses or as recovered values. Predominant among these are the application of storage tank controls for volatile petroleum products and the utilization of activated carbon for solvent recovery. The incentive for development has been heavily weighted for an economic return on investment rather than concern for environmental pollution control, although a number of instances have been reported recently in which pollution control applications have resulted in unexpected economic returns.

The most conspicuous lack of published data is in quantitative information relating to the effectiveness or efficiency of the various control techniques and equipment. The crux of the control evaluation problem was identified in a recently completed study of polycyclic aromatic hydrocarbons. Although specifically cited with respect to PAH emissions, the statement applies much more broadly. In their draft report on Control Techniques for Polycyclic Organic Matter Emissions, GCA Technology (1970), after considering the available design data, stated, "in the absence therefore of any practical information on the effects of existing types of gas cleaning equipment on polycyclic organic emissions, we must rely on theoretical considerations to determine which cleaning techniques will be effective in removing polycyclic organic emissions". Although the outlook for control technology for certain other hydrocarbon classes is not quite so bleak, the degree of effectiveness offered by a specific design for a specific emission is still uncertain in the best of cases.

Apparent control effectiveness may result, in many cases, from variable definitions of pollution or from failure to measure the process output under operative controls. An example is provided by Fawcett (1970) in a review of emissions common to the phthalic anhydride manufacturing industry and the type of controls used. Emissions are generally the acids or acid anhydrides, aldehydes, o-xylene or naphthalene, and occasionally, particulates. In one set of locations, the air pollution problem is that of nuisance odors and lachrymatory emissions, which are characteristic of the organic acid components. In West Coast locations or other areas of poor air shed ventilation, however, the pollution problem is caused by the photochemically reactive aldehyde and aromatic constituents. Fawcett reports that wet scrubbing affords 99 percent removal of the acids and anhydrides, but gives relatively poor control of aldehydes. Thus, in smog-prone areas where the aldehyde is of primary concern, "control" would involve incineration of the process off-gas, either by direct flame or catalytic methods; in other areas "control" would call for acid removal by wet scrubbing. The impact of control is therefore measurable only in the context of local pollution problems.

With a few exceptions, the hazards to health and welfare posed by organic compounds have not been fully determined. Until these basic parameters are defined, control effectiveness cannot be absolutely fixed. Thus, quantitative information on design and "efficiency" for existing control techniques can best be assembled on a "case history" basis.

In the following sections, the generally used control techniques are briefly reviewed and the economic costs of general case control techniques are presented. Detailed treatment of two areas of wet scrubbing technology is given in Appendices E and F, along with the calculations and other documentation supporting the general case economic evaluation summaries, presented in Appendices A through D.

B. CONTROL TECHNOLOGY

1. Emission Elimination Via Add-On Devices

a. Direct Flame Incineration

Control of hydrocarbon or organic emissions by incineration involves direct (non-catalytic) oxidation of the combustible portion of the effluent, the desired ultimate products of combustion being water and carbon dioxide. Effluent streams from incineration of organic emissions may be characterized as either fuel-rich or fuel-poor. Relatively few effluent streams are fuel-rich and they are more readily amenable to control. The dilute or fuel-poor effluent streams are of more concern, because of their ubiquity and because of the diversity of types and concentrations of organic species involved.

Fuel-rich effluents are most common in the petroleum and petrochemical industries and are generally handled by the so-called smokeless flares. Smokeless flares depend on three principal factors: (1) sufficient fuel values in the effluent stream to attain theoretical combustion temperatures, (2) sufficient combustion air, and (3) turbulent mixing of fuel and combustion air. Given a fuel-rich effluent, such as a highly volatile hydrocarbon waste stream from a refinery operation, factors (2) and (3) are generally accounted for by the use of steam injection, which provides a low-cost energy source for the inspiration of combustion air and for production of turbulent mixing. Steam also aids in combustion by reaction in the flame to form molecular species and radicals, which burn or decompose completely at relatively low flame temperatures.

The design and application of smokeless flares have been reviewed by Danielson (1967), Murray (1967), and Miller (1968), and rather generally in Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources (USDHEW, 1970).

The same controlling factors, listed for flare combustion of fuel-rich effluents influence the combustion of fuel-lean effluents. In these effluents, however, the effluent stream usually lacks sufficient fuel values to attain stable or self-sustaining combustion temperatures, and a secondary fuel source must be supplied. The most commonly used supplemental fuel for direct flame incineration is natural gas, although in some applications, petroleum-based fuels are used. In some industrial operations, waste organic gas streams are burned in existing boiler furnaces, but, because of increased problems in maintaining proper boiler performance, this technique has limited application.

For most hydrocarbon compounds, the lower limit of flammability corresponds to about 52 BTU/SCF, and waste gas streams are generally limited, for reasons of safety, to 25% of the flammability limit, or 13 BTU/SCF (Stern, 1968). Because of this necessary dilution to a level well below the flammability limit, additional energy is required to maintain combustion of the hydrocarbons; this energy is added by preheating and by supplementary fuel burners. The minimum temperature level required in afterburning is the autogenous combustion temperature. The other conditions necessary for complete oxidation include good mixing of the waste gas with the hot combustion gases and residence times of 0.3 to 0.5 second. The Air Pollution Engineering Manual (HEW, 1967) presents basic design procedures for direct-flame afterburners and provides data on stack analyses for diverse applications.

Although design methods present no particular engineering difficulty, the safety problems attendant on handling a gas whose components may lie in the explosive range often require the services of an engineering group specializing in combustion or furnace operations. With any incineration process, including afterburning, the principal factor, from an emission standpoint, is the degree of completion of the oxidation reactions. Even when incompletion of combustion is limited to 1 or 2% the result may be intermediate oxidation products whose intrinsic hazard or nuisance value is greater than that of the original hydrocarbons. The problem is then one of quality rather than of quantity. A case in point is the study published by Sandomirsky et al (1966) of the incinerative disposal of an odorous mineral oil aerosol fume created in rubber processing. Although direct-flame incineration was stated to yield 84-92% oxidative removal, "samples taken from the stack gas indicated a completely changed material, compared with samples from the inlet process gas ... Products indicated as being present in trace amounts in the stack gas were acids, anhydrides, lactones and unsaturates. These were due to thermal cracking and oxidation in the combustor". Whereas the mineral oil caused odors and visible fumes, the oxidation products were certainly more reactive smog-formers than was the precursor oil. Thus, although complete afterburning is an effective method for disposal of hydrocarbon vapors, incomplete and inefficient afterburning may create a pollution problem that is more serious qualitatively than that faced initially.

The open literature is replete with articles describing, in general qualitative terms, the application of direct flame incineration to a wide variety of sources. Very few of these reported studies, however, provide sufficient data to assess the performance of a particular system. Much of the art resides in the proprietary files of companies specializing in incineration equipment. Danielson (1967) reviewed and summarized much of the available information and provided some very helpful case studies. General engineering data on the combustion of organic gases may be obtained from such sources as the North American Combustion Handbook (1952). Waid (1969) presented some design considerations and limited laboratory test data on a specific burner configuration.

The design of afterburners for application to varnish cookers was considered by Mills (1959). Benforado (1968a) described five methods (including incineration) for controlling air pollutants from painting and baking operations in finishing plants. He also (1968b) presented data on the applicability of direct-flame incineration to wire enameling operations and to the paint industry (1967). Elliott (1962) performed an experimental program on control of organic emissions from protective coating operations. Wallach (1962) provided data on the combustion of gaseous effluents from baked lithograph coatings.

The main point brought out by these and other authors is that proper design and performance of direct-flame incineration equipment depends greatly upon knowledge of the type of organic species in the effluent stream and on adequate testing and monitoring to assure that the desired performance is achieved. With simple and easily combusted waste streams, minimum flame temperatures and residence times can achieve complete combustion. Complex and refractory waste emissions, such as those from the baking and heat treatment of vinyl and other organic-based plastic and polymeric coatings, may require long residence times at temperatures above 1600°F to assure satisfactorily complete combustion.

One of the primary advantages of combustion processes is that they generally convert the pollutant directly to nonnoxious substances. Sometimes, however, the organic contaminant contains constituents other than carbon, oxygen, and hydrogen which, when combusted, result in a product more noxious than the hydrocarbon itself. Organic substances containing sulfur and halogens are primary examples. With sulfur the product is SO_2, which is generally considerably less noxious than the organo-sulfur precursor. With halogens, the products are generally acid gases such as HCl, which can severely corrode the control equipment or can produce nuisance or corrosion problems outside of and adjacent to the industrial complex. In such situations, secondary purification, generally by liquid scrubbing, is used to remove inorganic compounds from the effluent.

In an improperly designed combustion system it is also possible that hydrocarbons are only partially oxidized and aldehydes are formed. Aldehydes are associated with smog formation and are more objectionable than the original hydrocarbon. The possibility of formation of benzo(a)pyrene, a known carcinogen, by controlled combustion is discussed by Boubel (1963).

Another disadvantage of combustion processes is the possible formation of nitrogen oxides. In attempts to increase the efficiency of combustion of hydrocarbons, the efficiency of oxidation of nitrogen increases, with the result that NO_x is added to the already existing NO_x burden produced by automobiles and by other stationary combustion sources.

A significant factor in direct-flame incineration is the cost of the secondary fuel. Because of insurance underwriters' restrictions, most waste gas streams are diluted to well below the flammable or explosive limits, usually below 25 percent of the lower explosive limit. In these cases, fuel costs can be high enough to require heat-recovery equipment. The wide variety of heat recovery systems now in use generally involve using the waste heat to preheat the effluent gas stream or to provide process heat to some other part of the operation. Careful evaluation of the total system is required to assess the cost effectiveness of direct-flame incineration in comparison with alternative control methods.

b. Catalytic Oxidation

As a means of atmospheric pollution control catalytic oxidation is applied most often to reducing or eliminating organic emissions where recovery of these emissions by regenerable processes is not warranted. Catalytic oxidation is thus applicable to dilute emission streams and to emissions that are difficult or impracticable to recover by other methods. Conventional flame incineration and catalytic oxidation are often quite competitive methods of emission control; careful engineering and economic evaluations are required for a proper choice of combustion methods. Several pertinent reviews of flame incineration versus catalytic oxidation have been made in recent years. Hein (1964) and Brewer (1968) compared the costs of installing and operating these two processes and showed that in many instances catalytic oxidation processes are more economical. Thomaides

(1971) also compared the costs and presented advantages and disadvantages of catalytic oxidation and direct flame incineration.

The literature dealing with comparative economics of incineration must be viewed with extreme caution, however, because presentation of the evaluation methods is often sketchy and incomplete, and sometimes a deliberate choice of examples tends to show a clear advantage for a particular control system.

The practical applications of catalytic oxidation in control of industrial solvent emissions remain highly proprietary. Literature is available, however, on application of catalyst combustion in paint manufacture (Stenburg, 1958), paint baking ovens (Danielson, 1967), insulation board manufacure (Duerden, 1965), and coffee roasting (Sullivan, 1965). Betz (1963) showed that catalytic combustion was the most efficient method of removing effluents from a phthalic anhydride plant. The Air Pollution Engineering Manual (Danielson, 1967) gives case histories with design data and operating conditions. Review articles such as those by Brewer (1968) give a limited amount of practical information on the choice of incineration techniques.

A significant advance in the art of catalytic incineration has been the development in recent years of improved catalyst support systems, namely honeycomb ceramics. An excellent article by Miller (1967) presents the results of a pilot scale study of several catalyst support systems. Measurements of oxidation efficiency over a range of temperatures and space velocities show clear advantages of honeycomb ceramics over other catalyst support systems.

Basic research on the susceptibility of homologous series of hydrocarbons to catalytic oxidation was carried out by Accomazza (1965) and Carretto (1966); the industrial aspects of design, economics, and operation were reviewed by Brewer (1968) and Werner (1968). Werner classified the commercial catalytic afterburning catalysts as (a) active metal/metallic carrier (b) active oxide/oxide carrier, and (c) active metal/oxide carrier. Poisoning is a major problem with catalyst beds, as is particulate plugging; both Brewer and Werner provided information on the nature of poisons for the various types of catalysts.

Effluents containing sulfur, halogens, and silicon are known to be poisons for platinum and palladium-type catalysts. Although the mechanisms are not fully known, silicon oxidizes to silica, which blocks the pores of the catalyst. Metal oxide catalysts developed for specific applications have been shown to be less susceptible to halogen poisoning than the precious metal catalysts. Other problems such as thermal degradation, however, limit the application of these systems.

The primary advantage of catalytic incineration is that extremely dilute concentrations of noxious organics can be oxidized with only small amounts of supplemental fuel being required, often only that needed to preheat the catalyst bed. Thus, the lower fuel costs present a significant advantage over direct-flame incineration for dilute waste gas streams.

Again, we emphasize that knowledge of the type and concentration of the waste gases being incinerated is required to select and design a properly performing catalytic system. In the past, improper application of catalyst systems resulted in installations that would not meet local code requirements for emission control. Recognition of these problem areas and more careful design studies are currently resulting in successful application.

c. Adsorption

Although a variety of high-surface-area materials have been used for vapor-phase adsorption, only activated carbon has been used widely in practical applications involving organic vapors. The great advantage of carbon over other adsorbents is its ability to strongly and regenerably adsorb a wide variety of organic molecules, even in the presence of water vapor.

Because the literature on the theory and application of activated carbon for adsorption of organics is voluminous, no attempt was made to review the subject completely. Thorough reviews have been presented in a number of standard texts, such as Mantell (1961) and Hassler (1963). In addition, commercial suppliers of activated carbons and carbon adsorption systems maintain extensive data files and cooperate in making available this specific information on design and operation.

Theoretical and experimental studies have been made to describe the various parameters influencing the operative cycle of adsorption-regeneration on carbon. Mathematical relationships correlating adsorptive capacity, bed life, and pressure drop with specific and generalized vapor properties, vapor concentrations, temperature, flow rate, and carbon properties have been reported. Perhaps the most useful relationship for preliminary screening of the applicability of carbon adsorption to a particular system is that based on the Polanyi potential theory, described and developed by Grant et al (1962) and Robell et al (1965).

The Polanyi potential, A, is related to temperature, concentration, and molar volume of adsorbate by the expression,

$$A = \frac{T}{V_m} \log \frac{C_o}{C_i}$$

where T = adsorption temperatures in °K
V_m = molar volume of liquid adsorbate at the normal boiling point in cm^3/mol
C_o = saturation vapor concentration
C_i = influent vapor concentration.

By experimentally determining the adsorptive capacity, q, of a particular carbon for several organic vapors over a range of A, a generalized semilog plot of q versus A may then be used to predict q values for other organic vapors.

Generalized curves of q vs A (such as given by Grant et al, 1962) for several typical carbons may thus be utilized to screen the applicability of carbon adsorption for the recovery of any known organic vapor in the concentration range of interest.

The application of carbon adsorption for solvent recovery, particularly where the vapor concentration is fairly high (>500 ppm) and the solvent has recovery value, is a standard operation. Integral, "packaged" systems are available from several commercial sources. A number of papers have been published on these applications as well as those involving removal of low concentrations of noxious vapors and, more recently, the concentration of vapors for subsequent incineration. Reviews on the elimination of organic vapors by carbon were given by Barnebey (1959) and Morgani (1951). Parameters associated with the operation of adsorption equipment were discussed by Chetfield (1967) and LeDuc (1967). Adsorption is used for the control of emissions from surface coating operations (Kanter, 1959; Elliott, 1961), pharmaceutical manufacture (Johnson, 1959), and solvent extraction operations (Barnebey, 1965).

Barry (1960), after reviewing the published information on carbon systems design, concluded that the design and scale-up procedures at that time were not satisfactory. Confirming this finding, the Los Angeles County Air Pollution Control District and the U.S. Public Health Service undertook the evaluation of adsorption design methods; they obtained and published updated design information (Elliott, 1961); much of which was incorporated by Danielson (1967).

The economics of operation of carbon adsorption systems are strongly influenced by the specific vapors adsorbed, the influent concentration, and the ease of regeneration. Steam is the usual medium used to strip the loaded carbon bed, but for some conditions the temperature range of saturated steam is not high enough to strip the sorption bed in a reasonable regeneration time cycle. Mattia (1970) stated that 3.5 lb of steam/lb of stripped organic is required when the influent vapor concentration is 0.2 percent by volume, whereas over 30 lb of steam/lb of organic may be required when the pollutant concentration is reduced to 200 ppm.

Because steam regeneration requires corrosion-resistant construction, capital costs are generally high. Capital costs were reviewed in Control Equipment, AIHA (1968), and data on operating costs were reviewed by Mattia (1970). Lee (1970) reviewed design and operating conditions of successful carbon adsorption systems.

Mattia (1970) presented some preliminary studies and costs of a process that utilizes carbon adsorption to concentrate hydrocarbon effluents for subsequent incineration. This technique should be useful for effluent streams having little or no economic recovery value, in that it allows incineration of a more concentrated stream from the carbon desorption, with concommitant lower incineration costs.

d. Adsorption

Absorption is distinguished from adsorption in that with absorption the sorbed species is physically transferred across the sorbent interface, while in adsorption the sorbed species is held, physically or chemically, at the interface. In effluent gas purification, the most commonly used absorbents are liquids, primarily water.

Even though wet scrubbing methods are widely used for removal of particulates and hydrocarbons, usually concurrently, assessment of current design methods and the state of technical development of wet scrubbing showed a very serious deficiency. This deficiency is examined in detail in Appendices E & F of this report. A technical literature review showed an unbridged gap between theory and field practice. There was no rationale for scrubber selection or design in the following problem areas:

(a) Removal of liquid hydrocarbon aerosols or of particulates in association with heavy hydrocarbon co-particles, particularly polynuclear hydrocarbons.

(b) Combustion gas scrubbing with secondary absorption of water-soluble oxidized hydrocarbons.

(c) Condensation (direct or indirect), followed by mist-filtration or scrubbing.

Thus, the need was obvious for an intensive critical examination of scrubber technology, re-evaluation of design approaches, and correlation of data.

At the outset of this systems study, it became apparent that the major stationary sources of hydrocarbon emissions were combustion processes. Invariably, such processes emit particulates in association with hydrocarbons. Power generation, incineration of solid wastes, and disposal of industrial organic liquid sludges are examples of such operations. Attention was focused on hydrocarbon-particulate emission because of the health problems attendant on the polycyclic aromatic hydrocarbons normally found in combustion off-gases, particularly in inefficient combustor units. Several of the polycyclic aromatics, notably benzo(a)pyrene (BaP), are known to be carcinogenic, and for this reason, control information for these hydrocarbons merits priority.

Hangebrauck (1967) measured rates of emission of polynuclear hydrocarbons in refuse burning and various industrial operations, both before and after the exhaust gases passed through control equipment. Data were presented on the effect of CO waste heat boilers and plume burners on catalytic cracking regenerators in petroleum refining, and of water-spray scrubbers and steam "sprays" in batch asphalt hot-road-mix plants. In the latter, water-spraying was found to be 92% effective in BaP removal; the data were extremely limited, however, and no information was given on the design of the control equipment.

Cuffe (1967) studied emissions of seven key polynuclear hydrocarbons from coal-fired power plants using various boiler designs. Preliminary tests showed that considerable recovery of the polynuclear aromatics was effected by the fly-ash collectors, although no quantitative data were provided. Full-scale tests showed that even some formaldehyde was removed with the particulates, an indication of probable adsorption. In terms of control relevance, this means that control of hydrocarbon emissions from a combustion process can and should be accomplished via control of particulates.

Appendix F presents results of a review of the performance characteristics of wet scrubbing devices in particulate removal. This presentation describes a novel correlating technique that shows unique promise as a tool for valid absolute performance comparison and establishes the test conditions necessary to validate such comparisons.

Briefly summarized, this study showed that performance of dispersed liquid wet scrubbers is mechanistically explained by turbulent agglomeration contacting and secondary inertial removal, rather than by inertial impaction theory. It was found that three primary independent variables control scrubber performance: inlet dust loading, water/gas ratio, and gas velocity (or pressure drop equivalent). Further, when scrubber performance was expressed in terms of the percent mass penetration*, the performance was inversely proportional to both inlet dust loading and the liquid/gas ratio. When the latter variables were combined into a single product group, termed the "agglomeration index", the literature data on dust penetration showed that penetration was inversely proportional to this agglomeration index. Application of this new concept to a wide variety of experimental and field data on wet scrubber performance showed that the agglomeration index can be a sensitive and powerful correlating parameter. Deviations of reported data from the correlation were found to be indicative of dust feed pre-agglomeration or design deficiencies in the removal mechanism (as distinguished from the contacting mechanism) of the scrubber.

The third independent variable, pressure drop, was readily correlated when performance data were plotted at constant agglomeration index conditions.

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* Percent mass penetration is defined as the weight percentage of inlet dust that penetrates the scrubbing device; the inverse of percent removal efficiency.

The final generalized equation obtained was:

$$\% \text{ Penetration} = \frac{K}{(Cd)(W/G)(\Delta P)^n}$$

where

K = performance constant
C_d = inlet dust loading, grains/CF
W/G = water/gas ratio, gallons/MCF
P = pressure drop, inches of water
n = 1 or 2, depending on pressure drop regime.

In Appendix E, new and hitherto proprietary design techniques are presented covering applications for the removal of soluble pollutants, such as partially oxidized hydrocarbons from waste incineration, in a combination gas quench-cooling operation.

2. Emission Elimination via Process or Equipment Modification

Reviews of pollutant sources and existing control technology have pointed out certain categories of hydrocarbon emissions and sources for which existing control techniques, per se, are not directly applicable (e.g. open burning of solid wastes). For these sources, reduction of emissions may best be accomplished, at least for the present and near future, by alternatives or process modifications.

a. Storage and Transfer Controls

Atmospheric emissions from storage and transfer of volatile organics, particularly petroleum products, have been identified as a significant source of organic pollutants. These emissions may be controlled by a variety of mechanical devices aimed at preventing the losses from occurring, rather than by systems for destroying or recovering emissions from deliberately vented waste streams.

Control methods for preventing losses of volatile hydrocarbons during storage and transfer were reviewed by Danielson (1967) and by USDHEW (1970). The American Petroleum Institute published an excellent series of technical bulletins covering methods of calculating losses and recommended practices for reducing or controlling emissions from storage and transfer of petroleum products.

A recent review by the Petroleum Committee of the Air Pollution Control Association (TI-3 Petroleum Committee, 1971) summarized the state of the art of storage tank controls.

The most generally applied control device for reduction of storage tank emissions is the floating roof storage tank. Although a variety of floating roof designs have been developed, all consist of an impermeable cover, which floats on the stored liquid and provides a sealing device between the floating roof and the tank wall to prevent evaporation.

Other devices, such as sealed or pressure tanks and vapor recovery systems, are used much less than floating roof controls. Vapor recovery systems are more commonly used in transfer operations, in conjunction with sealed and submerged filling devices, to prevent and recover both evaporative and spillage losses.

b. Waste Burning Alternatives

Sections II and III identified the disposal of solid wastes by open burning as a highly significant contributor to the total hydrocarbon emissions problem. The large number and widely dispersed distribution of individual point sources of waste disposal by open burning make the application of conventional control techniques prohibitive, both technologically and economically. The review of existing technology has identified three principal alternatives to the open burning of solid wastes: multiple chamber incineration, sanitary landfilling, and composting. Other potential alternatives, which are in various early stages of development, are touched upon briefly after discussion of the three principal methods.

Sanitary Landfilling - Of the three alternatives, landfilling is the most widely practiced in the United States. The general consensus is that at least 50 percent of the collected refuse in the United States is disposed of in landfill operations. Unfortunately, most of the current landfill operations would not meet the definition of "sanitary" as given by the American Society of Civil Engineers (1959). The National Solid Wastes Survey (1968) found that of 6,000 sites studied in detail, only 6 percent met minimum requirements for designiation as "sanitary landfills".

Provided proper design and control, landfill operations can be handled in a manner that meets sanitary requirements with essentially no air pollutant emissions. The cost and availability of adequate land areas must be considered in any comparison of landfills with other disposal methods; in some municipal areas, these factors present a distinct disadvantage. A recently reported study of remaining landfill life at 34 cities (Solid Waste Report, 1970) shows a range of from 0 to 25 years remaining life, with landfills in approximately half of the cities having less than 5 years remaining.

Although the costs of collection and transportation are significant factors in the total cost of any disposal system, landfill operations are generally most heavily affected by transportation costs. With the rapidly increasing 'sprawl' of most cities, land sites within reasonable hauling distances are fast diminishing. In a survey of 439 cities (Combustion Engineering, 1969) 90 cities, or about 20 percent, reported hauling distances of over 10 miles to the disposal site.

Thus, the feasibility of sanitary landfilling as an alternative method is highly dependent on site availability and hauling distance. Since these factors cannot be accurately generalized, specific studies are required for each area considered.

Multiple Chamber Incineration - Recent studies of disposal of municipal and industrial wastes indicate that technology is available for the satisfactory (from an air pollution standpoint) disposal of most wastes by incineration (A.D. Little, 1970; Engdahl, 1969; Combustion Engineering, 1969). Although development of municipal incinerators in the U.S. has lagged considerably behind European practice, recent developments have shown that with proper combustion chamber design and application of air pollution controls, the operation is technically feasible, with acceptable emission levels. Depending on the type of operation, a solid residue of 5 to 15 percent of the original waste volume must be disposed of by landfill or other ultimate disposal or reuse.

Application of incineration to the disposal of industrial solid wastes has been limited historically to those industries generating significant amounts of wastes having a reasonable fuel value. For example, the lumbering and paper pulp industries utilize large amounts of bark and wood wastes as fuel, generally admixed with conventional fuels such as fuel oil. Much of the so-called incineration of industrial wastes is accomplished in single chamber incinerators and conical or "tepee" burners, which are little more than confined open burning.

Application of incineration as a feasible disposal alternative will require the installation of modern, properly designed equipment and the establishment of meaningful, rigid standards of performance to accomplish the desired goal of reducing or eliminating organic and other air pollutant emissions.

Composting - Of the three principal alternatives, composting has undergone the least study in the U.S. and thus entails the greatest uncertainty as to practical application and realistic cost. Most, if not all, of the demonstration and "model" composting operations started in recent years have failed, primarily for two reasons. First, no steady market for the end product could be developed and, second, odors from the aerobic decomposition were not controlled.

The low organic content of typical American wastes requires significant segregation before composting and the addition of large amounts of nutrients to achieve an acceptable soil supplement or fertilizer. Some agricultural experts believe that compost can never be marketed competitively with the inorganic fertilizers.

Other Waste Disposal Alternatives - Other alternative disposal methods under study by various investigators involve the segregation of wastes into various fractions such as metal, paper, and plastic, and conversion or recycling to provide usable materials. The Bureau of Mines (1970) investigated conversion of garbage and organic wastes into usable petroleum substitutes. By heating the organic wastes to 400°C under pressure with CO and H_2O, crude petroleum products were obtained. No cost estimates were reported, but it was estimated that each ton of urban refuse could produce one barrel of low-sulfur oil by this process.

Much publicity has been given to numerous studies related to the recycling of wastes; with few exceptions, however, technological and economic feasibility is yet to be demonstrated.

Advanced methods of incineration and mechanical waste reduction are being investigated. These methods include pyrolysis, high temperature incineration, and mechanical shredding and baling for volume reduction.

The Solid Wastes Report (1970) described pilot plants using pyrolysis and high temperature incineration. At a 35 ton/day pyrolysis pilot plant, volume reduction of 94 percent was reported. Capital costs of a 1000 ton/day unit were estimated at $10 million and operating costs at $7.50/ton. Based on operation of a 100 ton/day high-temperature incineration pilot plant, volume reduction was reported as 97 percent, with capital costs estimated at $15,000/ton and operating costs at $6-$8/ton.

Cost Comparison of Alternative Solid Waste Disposal Methods - Accurate economic cost comparisons of the alternatives to open burning depend on a number of parameters that vary widely with locale. For most municipal regions, no one simple solution is generally applicable; detailed study of the many factors involved in a satisfactory systems mix of alternatives is required for realistic cost comparisons.

For our cursory analysis, a simple, hypothetical situation illustrates some economic variables. An urban region is postulated which can be serviced by a centralized collection and transfer depot. This depot serves as the starting point in our comparison, and thus we need not compute the costs of various collection modes.

The centralized collection depot provides 100,000 tons/year of mixed total wastes for ultimate disposal. Average hauling distances to the various disposal sites are postulated as 2 miles to incinerator site, 5 miles to composting site, and 10 miles to landfill site. Transportation costs are estimated at $0.15/ton mile plus $1/ton for dumping or transfer. Thus, comparative costs of transportation and transfer are:

Disposal Mode	Round Trip Distance (miles)	Transportation and Transfer Cost ($/ton)
Incineration	4	1.60
Composting	10	2.50
Landfilling	20	4.00

Incinerator cost studies were reported by A.D. Little (1970) for a number of existing types of installations in the capacity range near 400 ton/day. Battery limits for evaluation were standardized; water quenching and 99 percent efficient electrostatic precipitation were assumed. Operation was established at three shifts per day, 250 days per year. No waste heat recovery, byproduct credits, or residue disposal debits were assumed. Disposal costs range from \$4.47/ton for a continuous, horizontal cylinder incinerator to \$9.50/ton for a residue fusion (Dravo/FLK) type incinerator. A weighted average cost of \$5.50/ton is assumed for our analysis as being representative of incineration practice in the United States.

Both Combustion Engineering (1969) and Aerojet-General (1969) have analyzed landfill operations. For this analysis we used the generalized cost expression given by Combustion Engineering:

$$\text{Cost in \$/ton} = 0.50 + \frac{6{,}000}{\text{tons/yr}}$$

Thus, for 100,000 ton/year, the landfill cost is \$0.56/ton.

Not enough examples of composting disposal in the U.S. are available to allow estimation of average costs. Such variables as market acceptance of the product cannot be assessed. Aerojet-General reported unit costs of \$5/ton for a windrow operation and \$10/ton for a mechanical composter. Kupchick (1966) reported cost data from 14 foreign plants averaging \$4.55/ton. Combustion Engineering (1969) reported costs of foreign practices as ranging from 30 to 60 percent of the cost of municipal incineration. For our example, we selected a value of \$5/ton.

A cost of comparison of the three alternative disposal modes for our hypothetical example is summarized in Table VI-1.

Table VI-1 - Disposal Costs for Hypothetical Example - 100,000 tons/yr

	Transportation Cost		Disposal Cost		Total Cost
Disposal Mode	\$/ton	\$/yr	\$/ton	\$/yr	\$/yr
Landfilling	4.00	400,000	0.56	56,000	456,000
Incineration	1.60	160,000	5.50	550,000	710,000
Composting	2.50	250,000	5.00	500,000	750,000

A detailed investigation of a specific geographical area, with recommendations tailored to the community needs and practices was made by Aerojet-General (1969) in their study of Fresno, California. Specific costs developed for the various disposal and processing methods were generally higher per ton than those used in our example. For waste disposal in the Fresno area, the recommended systems mix consisted of essentially no incineration, composting of all suitable wastes, and landfilling of the non-compostable portion. The projected total cost for the year 2000 was about $14/ton (in 1967 dollars) for the total waste management program.

c. Solvent Reformulation or Substitution

Since the advent of Rule 66 in the Los Angeles area and, more recently, similar legislative codes in other areas, solvent reformulation has been an accepted and widely practiced alternative for controlling solvent emissions.

Organic solvent emissions can be significantly mitigated by using solvents with low vapor pressures or photochemical reactivities. These reformulations or substitutions are governed by three basic factors: 1) adaptability to an existing process or formulation, 2) solvent performance, and 3) economics.

Equipment and process modifications can be minimized by substituting solvents that are in the same chemical class as those originally used. The decreased vapor pressure of higher homologs in any organic series benefits air pollution control and may not require serious modifications to an existing process or formulation. Such a substitution does not eliminate emissions, however, since the physical and chemical characteristics of the original and the alternative solvents are often similar.

Standards for measuring solvent performance depend on the application. Solvency can be classified according to the aniline point, dilution ratio, or Kauri-Butanol number. Solvency is a basic measure of solvent performance, but paint formulations and solvent extractions are notable examples of applications in which other parameters are needed to measure solvent performance. Basically, solvent performance is measured by the amount of solvent necessary to dissolve, or otherwise carry, a unit amount of solute. This criterion is applied to all solvents, but must be adjusted in accordance with other standards for an overall evaluation of solvent performance.

Both adaptability and performance influence the economics of solvent reformulation. A complete economic evaluation would reflect influences from the initial production to final consumption. In commercial processes, production and maintenance costs are more concrete, and more easily predicted, than such variables as public opinions on air pollution control criteria.

Solvent producers now have solvent blends that can be used for comparison and compromise to suit most processes. Values for solvency and other chemical and physical characteristics are available for evaluation in any application.

Surface Coatings - Larson and Sipple (1967) published some experimental data and guidelines for reformulating paints to conform to Rule 66. This report can be summarized by the statement that oxygenated hydrocarbons appear to be the most promising alternatives for paint solvent reformulations at the present time. C_4 through C_9 ketones have been mixed in various proportions to develop desirable paint solvent characteristics, often in mixtures with other oxygen-containing solvents. Oxygenated hydrocarbon solvents can be substituted into existing paint production equipment without excessive modifications, and these mixtures will usually meet solvency requirements.

Solvent reformulation has been used successfully to reduce the photochemical reactivity index of oil-base paint solvents. As yet, however, no solvent mixtures have been prepared which can combine low photochemical reactivity with solvent properties equal to those of the reactive aromatic hydrocarbons.

Oil-base paints enjoyed a monopoly of the industrial surface coatings market, until recently. Industrial coatings such as machinery paints, paper and wire coatings, wood preservatives, marine paints, and traffic paints were dominated by hydrocarbon solvents. The variety of problems involved in developing solvent reformulations for such diverse applications has required a considerable amount of research.

A more recent advance in reformulation has been the development of water-base paints. The advantages and variations available in this class of paints were described by Parker (1967). Applications for water-base paints are being continually developed, and they have become an influential substitute for oil-base paints in architectural (trade sales) application.

Substitution of water as the main solvent does not eliminate the problems of hydrocarbon emissions, however. Most film-forming polymers are based on carbon chains, which are insoluble in water. Water-solutions or emulsions of these materials require the suspension of unstable, partially polymerized species composed of molecules such as vinyl chloride, butadiene, acrylonitrile, methyl, ethyl and butyl acrylates, and glycerol derivatives. Solution or suspension of these resins in water also requires emulsifying agents such as dibutyl- and dioctyl-phthalate, hexylene glycol, esters of fatty acids, and paraffin waxes. In addition, fungicides and other preservatives must usually be included in water-based formulations.

We found in the literature no data on experimental measurements of emissions from water-base formulations. Empirical evaluations indicate that the excess of water in these formulations should preclude hydrocarbon pollution problems, but these evaluations may overlook the reactivity of hydrocarbons present in these mixtures. In general, the volatile hydrocarbon content of water based formulations is in the range of from 3 to 5 percent.

Degreasing - Solvent degreasing is widely practiced in the cleaning and processing of metal surfaces for such operations as salvage and repair, plating, and surface coating. Many of the smaller, non-automated operations utilize liquid-phase solvent degreasing, either cold or hot; most larger production and processing facilities utilize vapor-phase degreasing.

A wide variety of solvents used in small shops for liquid-phase degreasing ranges from gasoline and kerosene to the chlorinated hydrocarbons. These small operations are almost always uncontrolled and types and amounts of emissions are impossible to assess.

Until the application of Rule 66 in Los Angeles and similar regulations in other areas, the predominant solvent for vapor degreasing was trichloroethylene. In unregulated areas, it still accounts for the majority of applications. A review of studies made by one of the major industries using trichloroethylene was reported by the Aerospace Industries Association (1968). In order to comply with the Rule 66 classification of trichloroethylene as a non-exempt solvent, studies were made of the feasibility and economics of alternative procedures. These studies included testing of alternative organic solvents, testing of aqueous cleaning solutions and economic evaluation of possible control techniques and equipment modifications.

The investigation of alternative organic solvents resulted in selection of inhibited 1,1,1-trichloroethane as a satisfactory replacement for trichloroethylene. The physical and chemical (solvent and corrosive) properties of these two solvents are quite similar, 1,1,1-trichloroethane having a slight heat requirement advantage due to its lower vaporization temperature (166°F versus 188°F for trichloroethylene). This may be offset by higher vaporization losses for the more volatile 1,1,1-trichloroethane.

Detailed economics of controlling emissions by equipment modification and control devices were not reported. Estimates from four suppliers were given, however, ranging from $70,000 to $170,000 per degreaser, with no guarantee of meeting Rule 66 compliance.

The reported investigation of the use of aqueous cleaning solutions as alternatives to vapor degreasing included an economic comparison of the two methods. The comparison summary, shown in Table VI-2, is for comparably sized facilities. The aqueous system requires, in addition to the cleaning solution tank, a rinse tank and drying oven, which are not required for the vapor degreaser. Aqueous solution and rinse tanks were heated to 165°F, while the drying oven operated at 150°F. Solvent costs were based on a price of $1.20 per gallon, and an industry average usage loss of 1/2 gallon per day per square foot of tank top opening. Usage of the aqueous cleaning compound was based on complete renewal each month, with 15 percent makeup additions during the month. Labor costs are not included in the comparison, since these probably would be nearly identical.

C. ECONOMIC ASPECTS OF HYDROCARBON EMISSION CONTROL

1. General

As a result of the review of emission control technology, several systems were identified as being specifically pertinent to the control of hydrocarbon emissions from stationary sources. Additionally, the study of sources and their emissions identified and ranked those categories of sources which, if controlled, would result in the greatest benefit by reduction of emissions. In order to assess the economic impact of emission control of these various sources and to provide a frame of reference for evaluation of other control methods or alternatives, engineering cost studies were made for four types of control schemes: gasoline storage control, waste gas incineration, adsorption, and wet scrubbing.

Table VI-2 - Typical Comparative Cost Data: Solvent Vapor Degreasing Versus Aqueous Cleaning

	Aqueous Degreasing	Solvent Degreasing
Basic Equipment		
Aqueous - 2 tanks + drying oven, including heating and exhaust systems	$4050	
Degreaser + still + exhaust		$3050
Floor space $15/sq ft - Aqueous	3600	
- Degreaser		1500
TOTAL FACILITIES COST	$7650	$4550
Operating Costs (21-day month, 24-hour day)		
Solution cost - Aqueous	600	
Degreasing solvent cost		504
Heating - steam 15 psi at $1.50/1000 lb		
Aqueous - 2 tanks - heat loss	173	
Drying oven	45	
Degreaser - Vaporizing solvent + heat loss + still		117
Water cost - $0.14/1000 gallons		
Aqueous - Changing water in rinse tank each 2 hours	53	
Degreaser and still - Cooling water		55
TOTAL OPERATING COST	$871	$676

Note: Based on facilities 10 feet long by 4 feet wide by 7 feet working depth.

2. Gasoline Storage Control

Evaporative losses from the storage of gasoline and other volatile petroleum and petrochemical liquids constitute a significant portion of the total hydrocarbon emissions from industrial sources. The general case of control of gasoline storage losses was chosen to illustrate the economic costs of such emissions.

a. General Case Description

Control costs for pontoon floating roof tanks and fixed roof tanks with retro-fitted internal floating covers were compared with costs for conventional cone roof or fixed roof tanks. Three tank sizes were selected to cover the range of general operating practice: 50,000; 100,000; and 150,000 barrel capacity.

b. Installed Capital Cost

Total installed costs for the three tank types were obtained by adding estimated values for excavation, foundation, electrical grounding, piping, and painting to the average of installed-cost quotes provided by tank vendors. An allowance for engineering was also included in the total. These estimated costs are tabulated in Table VI-3 and plotted in Figure VI-1. A cost breakdown consisting of vendor quotes and construction cost estimate sheets is presented in Appendix A.

The total installed prices of the fixed or cone roof tank and the converted cone roof tank with internal floating cover are the lowest and highest costs, respectively; the total installed cost of the pontoon floating roof tank lies between these two. These prices indicate that for a new installation, it is less expensive to install a pontoon roof tank than a fixed roof tank with an internal floating cover for a gasoline vapor emission control. Where a means of emission control is required for existing fixed roof tanks, however, the addition of an internal floating cover is the most economical conversion. According to tank manufacturers contacted, conversion cost of removing the cone roof and installing a pontoon roof in its place is roughly twice the cost of adding an internal floating cover.

c. Operating Costs

Annual operating costs for each type of tank were taken to consist of the following:

Table VI-3 - Estimated Installed Costs of Gasoline Storage Tanks

Nominal Tank Capacity, Barrels	50,000	100,000	150,000
Size	90' dia x 48'	120' dia x 48'	150' dia x 48'
Installed Costs, $			
Fixed Roof Tank	161,000	257,000	379,000
Pontoon Floating Roof Tank	176,000	279,000	403,000
Internal Floating Cover in Existing Roof Tank	34,000	54,000	68,000

NOTE: Installed cost estimates are developed in Appendix A.

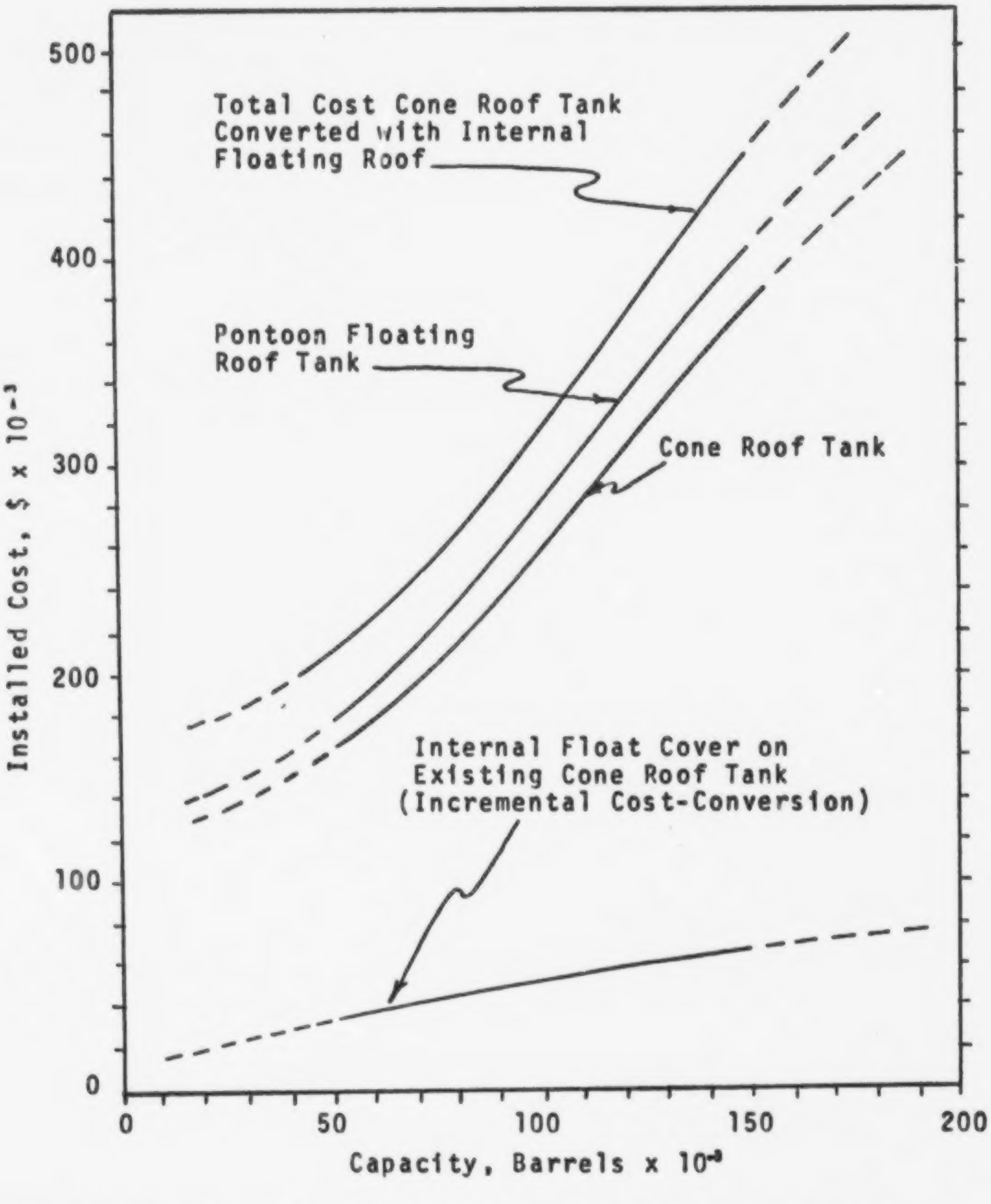

Figure VI-1 - Estimated Installed Cost of Gasoline Storage Tanks

Maintenance @ 2% Capital Cost

Depreciation @ 10% Capital Cost

Property Taxes @ 1% Capital Cost

Insurance @ .5% Capital Cost

Corporate Overhead @ 3% Plant Level Cost

Gasoline Loss @ $5.50/Barrel or $.131/gal.

Loss Calculations

Gasoline losses for fixed roof and pontoon floating roof tanks were calculated in accord with loss equations presented in American Petroleum Institute publications. Losses for fixed roof tanks with internal floating covers were calculated as a percentage of the losses determined for equivalent fixed roof tanks.

d. Evaluation of Storage Costs

Evaporation losses calculated for gasoline storage tanks are summarized in Table VI-4. Loss values were obtained by assuming Reid vapor pressure at 9.0 PSIA, tank outage (height of vapor space above liquid) at 50 percent or 24', and tank location at Philadelphia, Pennsylvania. Meteorological data presented at API Bulletin 2513 were used as required. The pontoon floating roof, internal floating cover conversion, and fixed roof storage systems, in that order, are decreasingly effective in reducing vapor emissions.

Operating costs are summarized in Table VI-5 and Figure VI-2 on an annual basis as total cost and cost per 1,000 barrels of capacity. Manufacturing estimate sheets for development of operating costs are included in Appendix A. In general, the highest operating costs occur in the type of storage system which exhibits the highest vapor loss, and vice versa.

An incremental capital investment vs operating cost analysis, which uses the fixed roof tank system as a basis for comparison, is illustrated in Table VI-6. A payout* of 2 to 4 years is realized for the additional capital required to construct a new pontoon floating roof tank instead of a fixed roof tank. Where internal floating covers are in-

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* Payout (in years) = capital cost/after tax savings plus depreciation, thus estimated payout is critically dependent on choice of depreciation rate.

Table VI-4 - Summary of Estimated Gasoline Losses

Tank Capacity (Bbls)	50,000	100,000	150,000
Fixed Roof: Bbl/yr	1,365	2,345	3,560
Gal/yr	57,300	99,500	149,500
Pontoon Floating Roof: Bbl/yr	98	150	205
Gal/yr	4,120	6,300	8,820
Fixed Roof/Internal Floating Roof: Bbl/yr	273	469	712
Gal/yr	11,450	19,600	29,800

NOTE: Gasoline losses are calculated in Appendix A.

Table VI-5 - Summary of Estimated Operating Costs For Gasoline Storage Tanks

Tank Capacity, Barrels	50,000	100,000	150,000
Annual Operating Costs, $			
Fixed Roof Tank	29,900	48,600	72,200
Pontoon Floating Roof Tank	25,000	39,500	57,100
Internal Floating Cover (In Fixed Roof Tank)	28,600	45,600	66,000
Annual Operating Cost/Capacity, $/1,000 Barrels			
Fixed Roof Tank	600	490	480
Pontoon Floating Roof Tank	500	400	380
Internal Floating Cover (In Fixed Roof Tank)	570	460	440

NOTE: Operating costs are developed in Appendix A

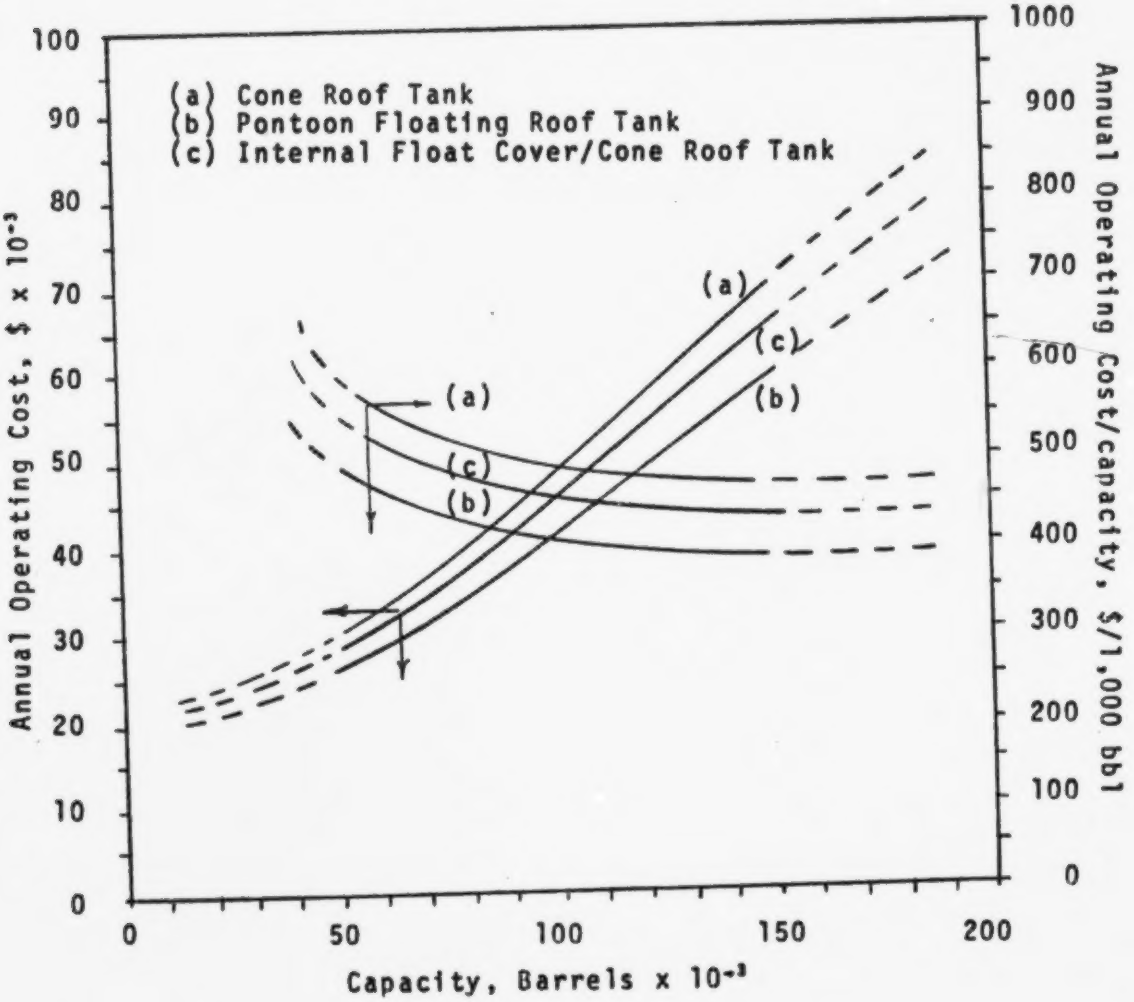

Figure VI-2 - Estimated Operating Cost of Gasoline Storage Tanks

Table VI-6 - Differential Savings Vs Differential Capital Investment and Payout (Base Case - Fixed Roof Tank)

Tank Capacity, Barrels	50,000	100,000	150,000
Pontoon Roof			
Differntial Installed Capital Cost, $	15,000	22,000	24,000
Differential Net Savings (Before Tax), $	4,900	9,100	15,100
Differntial Tax, @ 50%, $	2,450	4,550	7,550
Differntial Savings (After Tax), $	2,450	4,550	7,550
Payout After Taxes (yr)	3.80	3.26	2.41
Internal Floating Cover in Existing Fixed Roof Tank			
Differential Installed Capital Cost, $	34,000	54,000	68,000
Differential Net Savings (Before Tax), $	1,300	3,000	6,200
Differential Tax @ 50%, $	650	1,500	3,100
Differential Net Savings (After Tax), $	650	1,500	3,100
Payout After Taxes (yr)	8.40	7.83	6.87

stalled in existing fixed roof tanks to control vapor emissions, payouts based on gasoline savings are much longer. This method, however, is more economical than converting the fixed roof tank to a pontoon floating roof tank, in which case no payout exists at all. This statement is supported by the cost data in Appendix A, assuming a tank conversion cost double that for the internal floating cover.

3. Waste Gas Incineration

Because of the wide variety of sources and emissions controlled by both thermal and catalytic incineration, the choice of a representative general case system was somewhat arbitrary. For our evaluation of incineration, both thermal and catalytic, we chose an example, given by Danielson (1967), of a paint bake oven operating on a surface coating production line.

a. General Case Description

The emission source being controlled by incineration is a paint bake oven exhausting an air stream at 375°F, containing a 50/50 weight percent mixture of benzene and hexane. The oven was assumed to operate two shifts per day, 365 days per year. The range of operating variables included oven exhaust volumes of 1,000 SCFM, 10,000 SCFM, and 20,000 SCFM and total organic vapor concentrations equivalent to 15 and 25 percent of the lower explosive limit (LEL).

For the 50/50 benzene/hexane mixture the calculated LEL is 1.2 percent by volume. Thus, the 15 and 25 percent LEL levels are equivalent to 0.18 and 0.30 percent by volume.

Cost comparisons are made for cases of no heat recovery, primary heat recovery, and primary plus secondary heat recovery.

The design parameters for the thermal incinerator were a residence time of 0.5 second and an exhaust temperature reported by Danielson (1967) to give 90 percent conversion of hydrocarbons and carbon monoxide to carbon dioxide. For the catalytic incinerator, the oven exhaust gas was preheated to 650°F and the incinerator exhaust design temperature range was 1000° to 1200°F.

Reaction kinetics computations performed by one incinerator vendor (shown in Appendix B) indicate that catalytic conversion of the hexane/benzene system at 25 percent LEL is highly difficult because of the presence of hexane. This is generally true of most higher carbon aliphatic compounds. Under these conditions satisfactory conversion usually requires that the catalyst surface area be increased or the space velocity be reduced as much as possible. However, sufficient turbulence must be maintained to assure uniform combustion. The aliphatic aromatic system of hexane/benzene is chosen because it is typical of paint system diluents (e.g., naphthas may have 30% or higher aromaticity level), and because it entails considerations that are significant in selecting an incineration system.

Schematic diagrams of the systems without heat recovery are shown in Figures VI-3 and VI-6.

b. Heat Recovery

Primary, and primary with secondary, heat recovery systems were incorporated in the catalytic and thermal incineration systems and evaluated over the ranges of exhaust capacity and concentration specified for the basic incinerators.

The primary heat recovery process consists of utilizing a heat exchanger to transfer heat from incinerator exhaust gases to oven exhaust gases, which are being fed to the incinerator.

Secondary heat recovery is defined as the process in which incinerator exhaust gases cooled by primary heat exchange are used to heat make-up air being fed to the baking oven.

The heat recovery processes substantially reduce, and in some cases eliminate, the fuel required to heat the oven exhaust and makeup streams to required temperature levels.

Thermal efficiencies between 45 percent and 47 percent were specified with equipment vendor's order-of-magnitude quotes for primary heat exchangers. These values were also applied to secondary heat recovery systems. Thermal efficiency was defined by the equation:

$$\text{Percent Efficiency} = \frac{t_2 - t_1}{T_1 - t_1} \times 100$$

t_1 = Entering cold stream temperature, °F
t_2 = Leaving cold stream temperature, °F
T_1 = Entering hot stream temperature, °F

Process schemes for thermal and catalytic incinerators with primary heat recovery are shown on the flow sheets in Figures VI-4 and VI-7, respectively.

Thermal and catalytic incinerators with primary and secondary heat recovery are shown in the flow sheets of Figures VI-5 and VI-8. The additional fan used to handle make-up air is included to account for pressure drop in the exchanger and make-up air line.

c. Installed Capital Cost - Incineration

The total installed capital costs for thermal and catalytic incineration systems were based on written and verbal quotes received from two vendors and given in Appendix B. Each vendor quoted for both types of incinerators at one of the concentration levels, 15% LEL or 25% LEL, investigated. Within the scope of this study, these quotes were interpreted as being consistent with each other, or as provided by a single vendor. This assumed consistency of quotations was based on one vandor's additional quote which was in reasonable agreement with his competitor's prices for three systems. The quotations cover the majority of incineration systems with and without primary heat recovery. Estimates for secondary heat recovery systems were computed by utilizing plots of vendors' quotes, and assuming the following for secondary heat exchangers: a) thermal efficiency of 45 percent, b) overall heat transfer coefficient of 5.0 Btu/hr ft^2 °F, c) cost curve of the form, $f(x) = Ax^{.56}$ where

$f(x)$ = Cost, \$
A = Constant
x = Heat Exchanger Area, ft^2

Quotations also included vendors best estimate for installation cost as a percentage of capital equipment cost. Fifty percent was used for the integral erection of a process and a control system. One hundred percent was used for a retrofit. Installation included costs for excavation, foundations, piping, ductwork, insulation, electrical, painting, and engineering. Total installed costs of incinerator systems are presented in detail in Appendix B on construction cost estimate sheets. Values for 15 percent and 25 percent LEL systems over a capacity range of 1,000 SCFM to 20,000 SCFM are summarized in Table VI-7 and VI-8 and plotted in Figures VI-9 and VI-10, respectively.

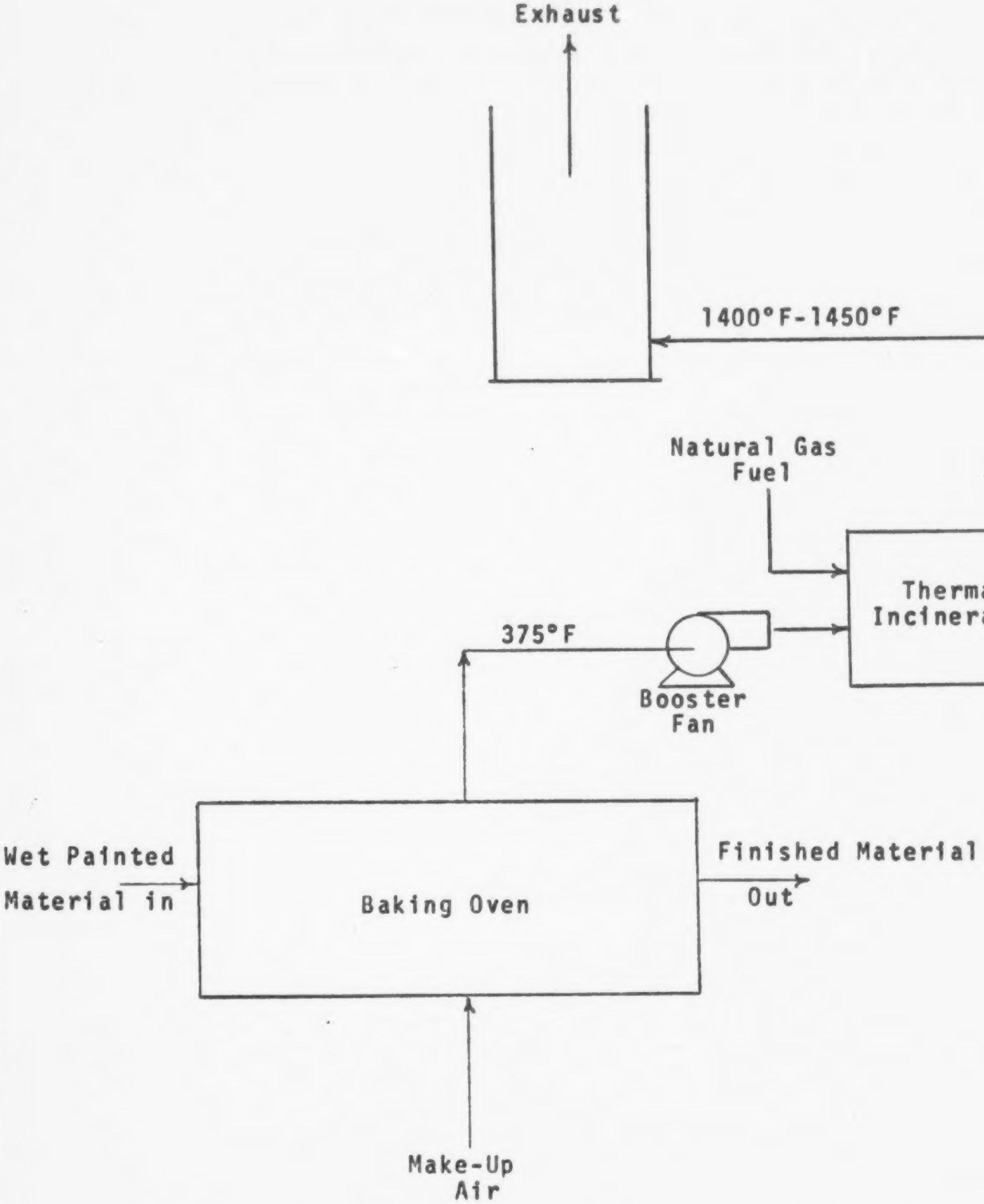

Figure VI-3 - Thermal Incinerator Without Heat Recovery - Flow Sheet

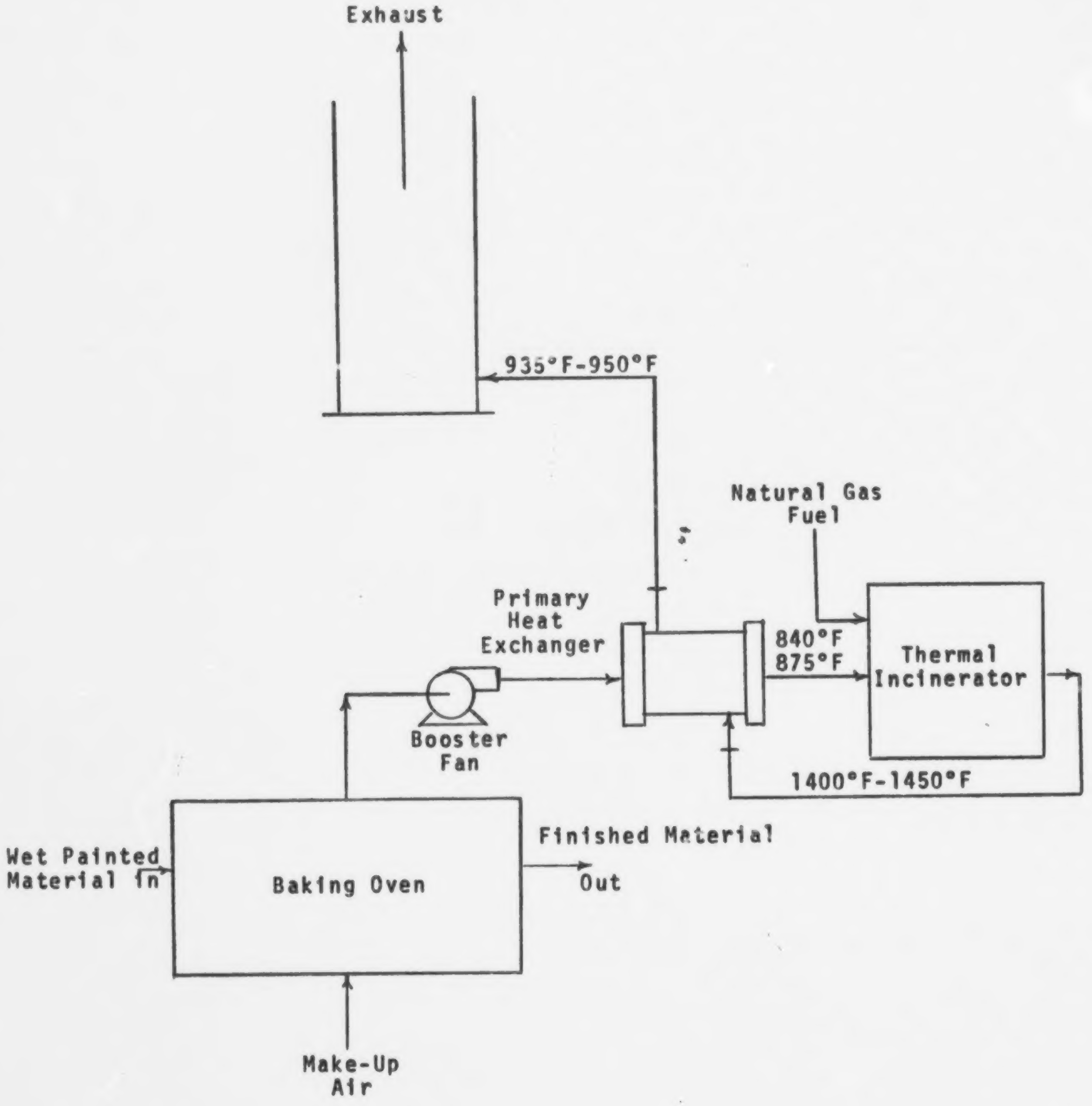

Figure VI-4 - Thermal Incinerator With Primary Heat Recovery - Flow Sheet

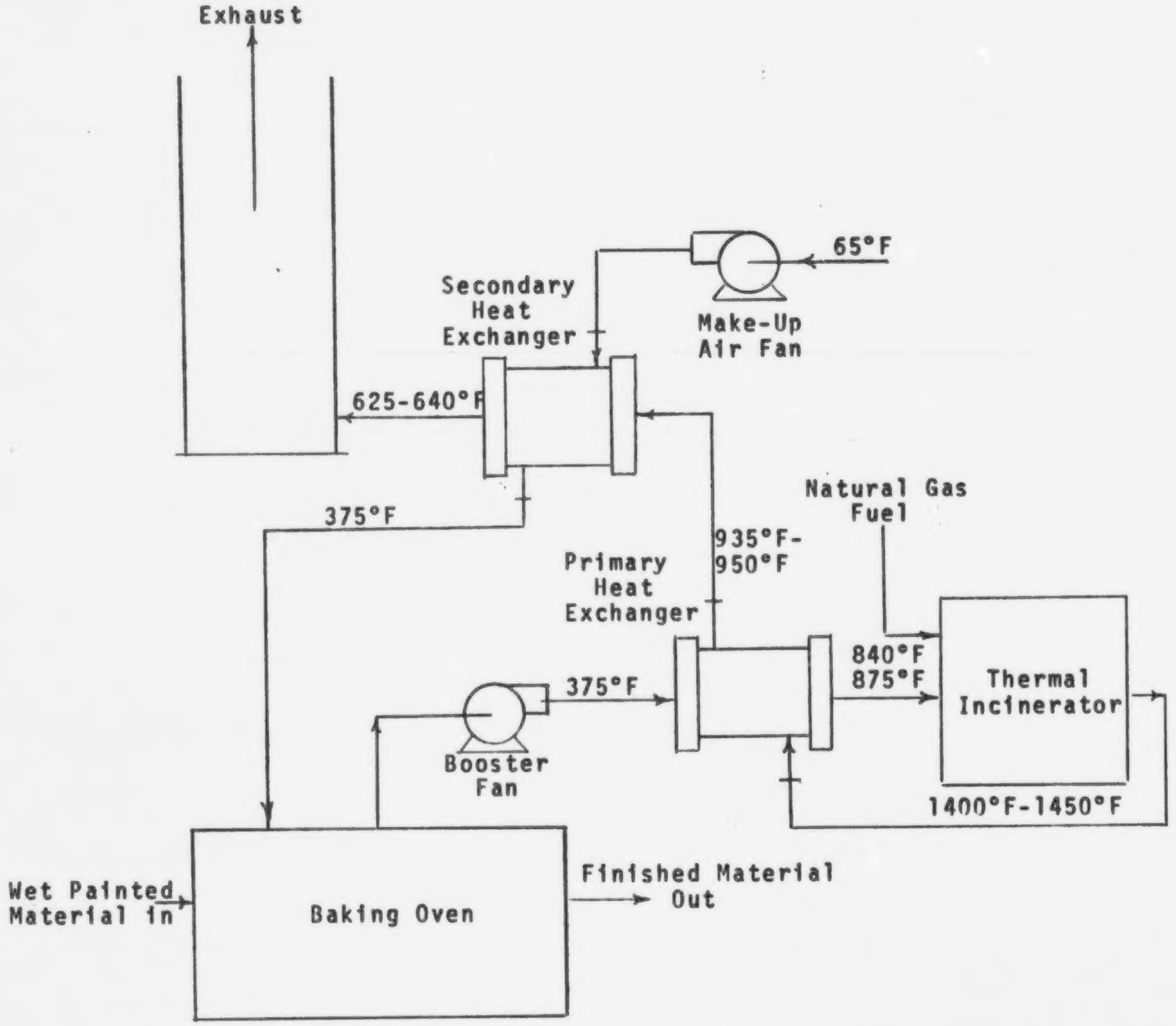

Figure VI-5 - Thermal Incineration With Primary and Secondary Heat Recovery - Flow Sheet

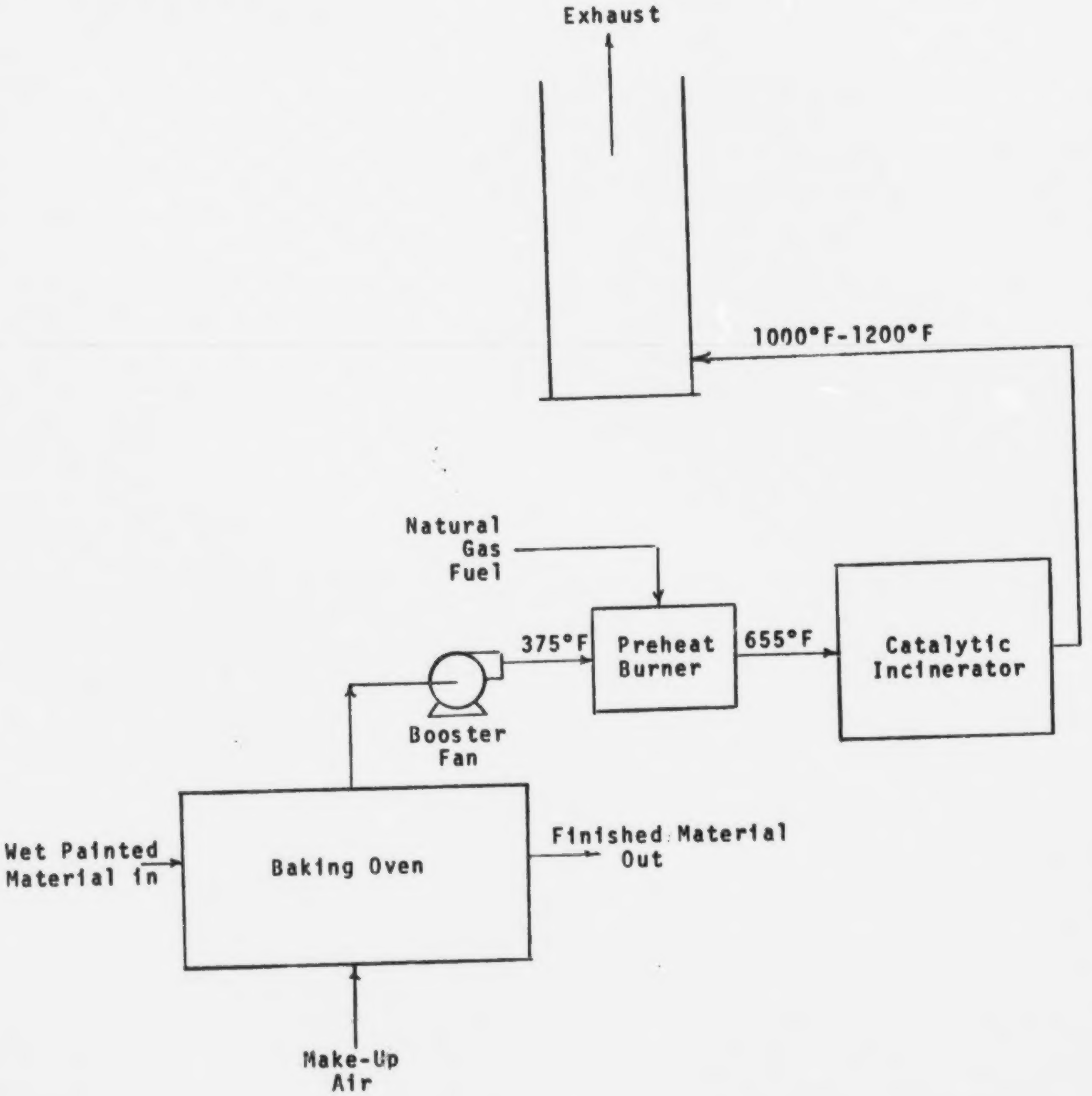

Figure VI-6 - Catalytic Incinerator Without Heat Recovery - Flow Sheet

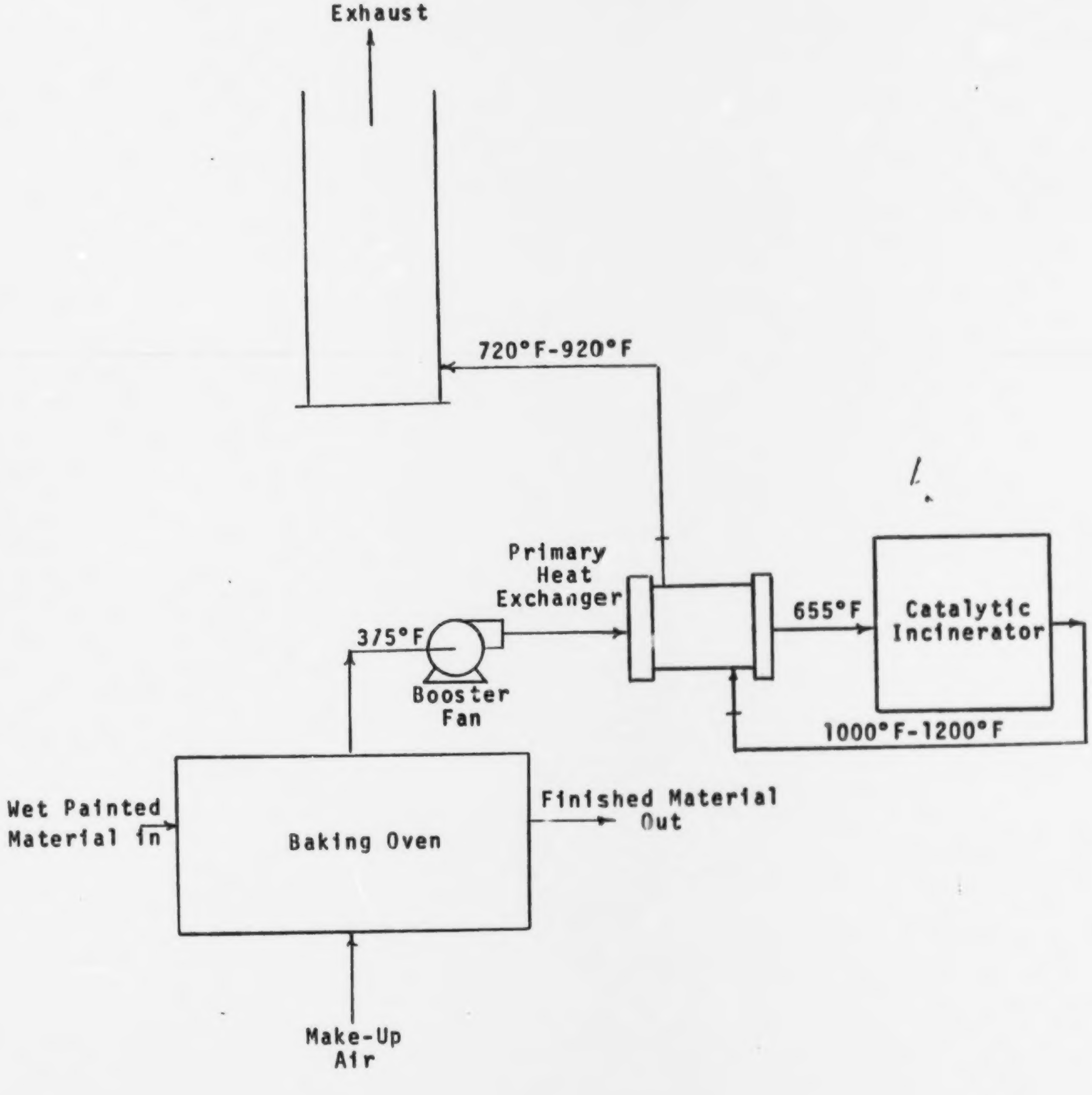

Figure VI-7 - Catalytic Incinerator With Primary Heat Recovery - Flow Sheet

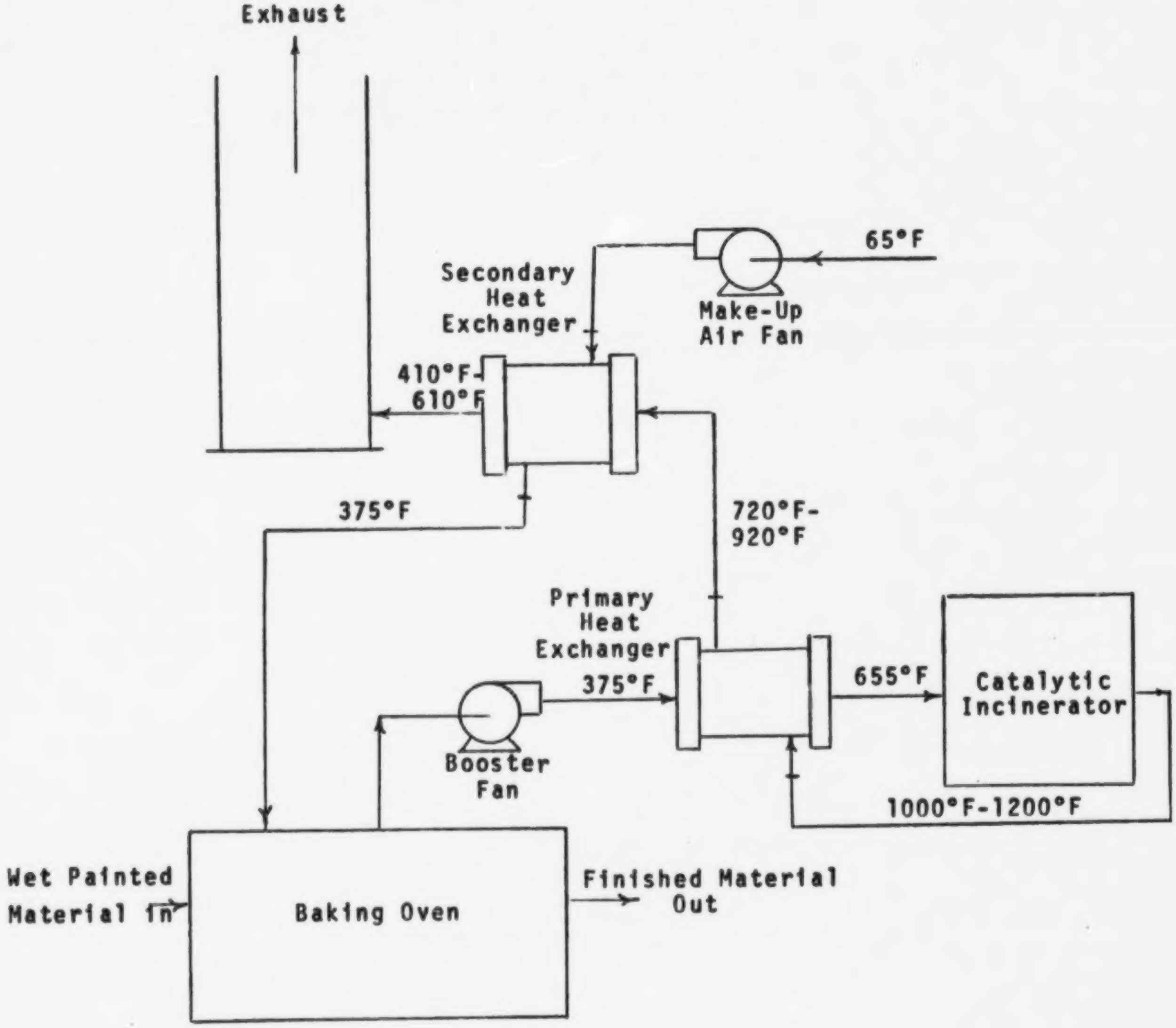

Figure VI-8 - Catalytic Incinerator With Primary and Secondary Heat Recovery - Flow Sheet

Table VI-7 - Estimated Installed Costs Thermal and Catalytic Incinerators - 15% Lower Explosive Limit

Incinerator Capacity, scfm	1,000	10,000	20,000
Installed Costs, $			
Catalytic without Heat Recovery	22,300	60,900	91,400
Catalytic with Primary Heat Recovery	39,600	121,800	182,700
Catalytic with Primary and Secondary Heat Recovery	60,700	196,900	295,400
Thermal without Heat Recovery	20,300	40,600	50,800
Thermal with Primary Heat Recovery	37,600	101,500	142,100
Thermal with Primary and Secondary Heat Recovery	53,600	158,300	228,400

Table VI-8 - Estimated Installed Costs Thermal and Catalytic Incinerators - 25% Lower Explosive Limit

Incinerator Capacity, scfm	1,000	10,000	20,000
Installed Costs, $			
Catalytic without Heat Recovery	32,500	203,000	376,000
Catalytic with Primary Heat Recovery	40,400	228,400	428,300
Catalytic with Primary and Secondary Heat Recovery	51,000	270,000	497,400
Thermal without Heat Recovery	20,300	69,000	102,500
Thermal with Primary Heat Recovery	30,100	107,600	173,600
Thermal with Primary and Secondary Heat Recovery	40,600	149,200	240,600

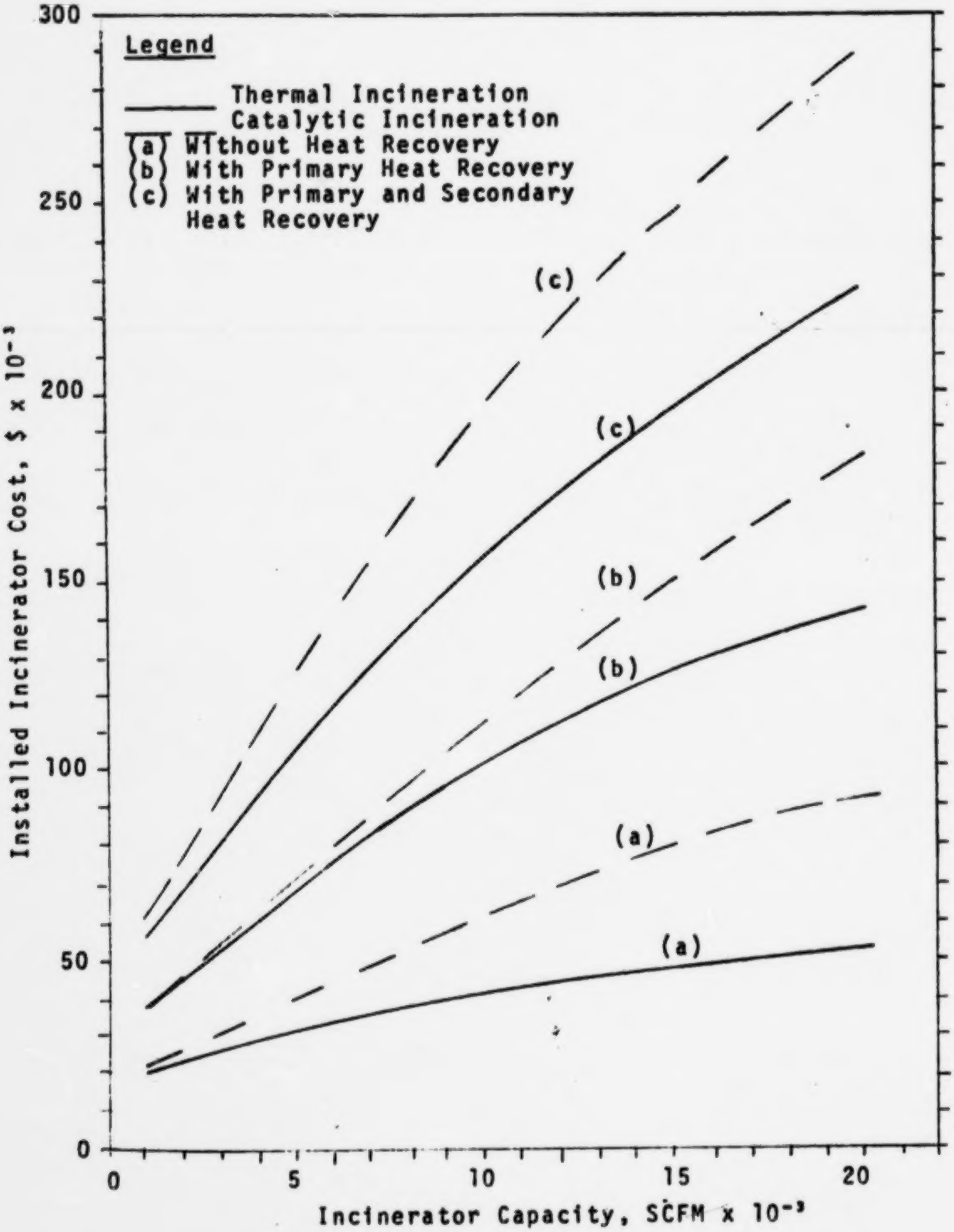

Figure IV-9 - Estimated Installed Incinerator Cost-15% LEL (90% Combustion of 50/50 - Hexane/Benzene Mixture @ 15% Lower Explosive Limit)

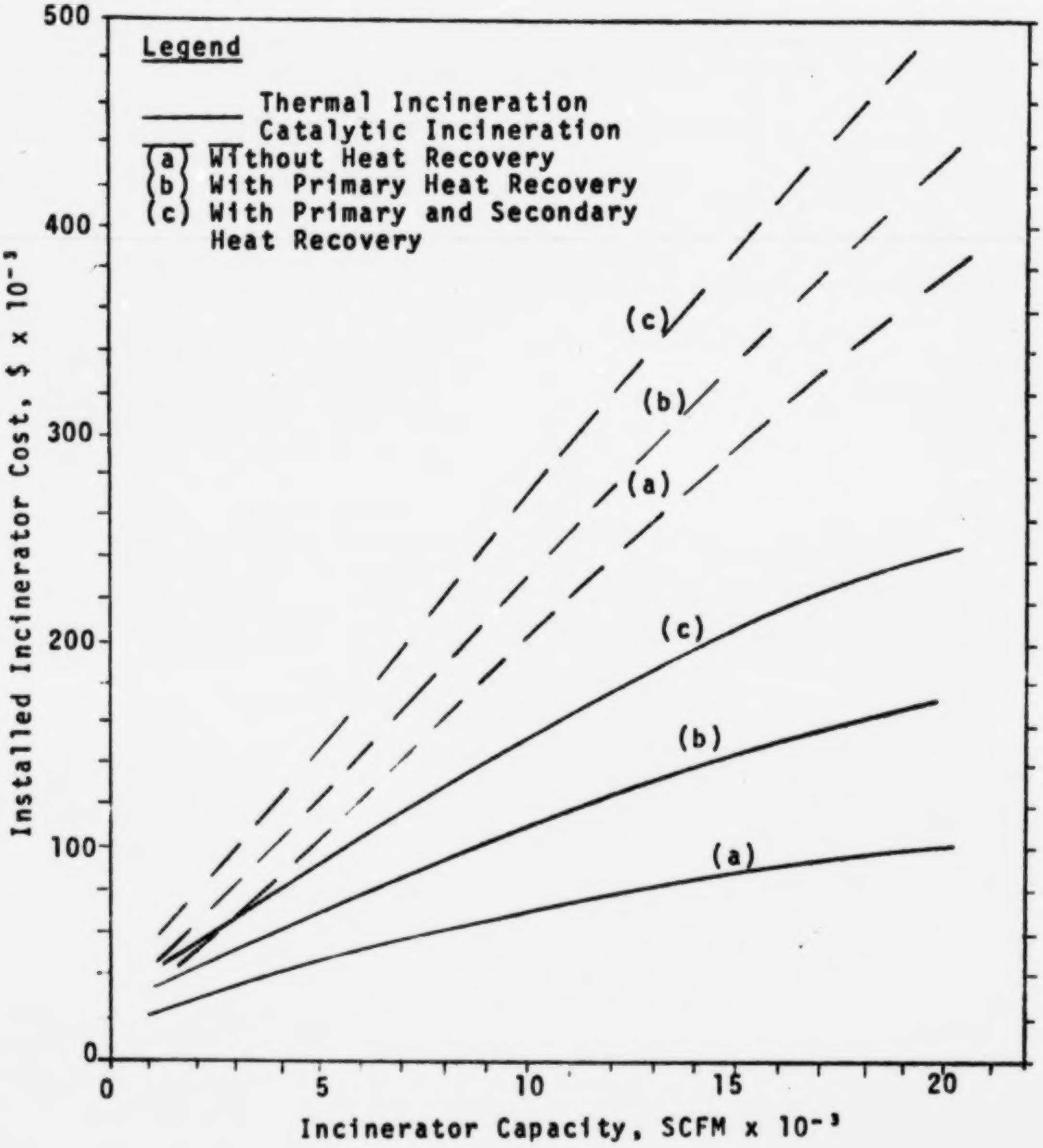

Figure IV-10 - Estimated Installed Incinerator Cost-25% LEL (90% Combustion of 50/50 - Hexane/Benzene Mixture @ 25% Lower Explosive Limit)

Analysis of these data indicated that total installed costs of catalytic incinerator systems are higher than those of thermal incinerator systems over the concentration and capacity ranges studied. Moreover, as concentration and capacity increase, the cost difference of catalytic over thermal incineration increases.

It is generally accepted that installed cost for a given incineration method increases with concentration level. However, exceptions to this appear in cases of thermal incineration with heat recovery systems at low volume capacities. This discrepancy may be the result of reduced burner and heat exchanger sizes or invalidity in extrapolating budget quote prices to low capacities.

A reduction in burner size occurs when the stream's thermal value or concentration increases at a given capacity. Heat exchanger surface area becomes smaller when temperature driving force is increased, as is the case with the higher exhaust temperature of the thermal vs catalytic incinerators.

Extrapolation of the data presented indicates that installed costs of both types of incineration, when compared on an equal flow rate basis, are the same at a point between 10 percent and 15 percent LEL concentration. Above this concentration range, thermal systems are economically favored; catalytic systems are favored at lower concentrations.

d. Operating Cost - Incineration

Operating costs for incineration control processes were calculated on the manufacturing estimate sheets included in Appendix B. The values were determined by incorporating the following percentages and rates in the calculations:

Operating - 2 shifts/day, 365 days/year, 0.5 man hour per sjoft direct labor

Maintenance @ 5% Capital Cost

Depreciation @ 10% Capital Cost

Property Taxes @ 1% Capital Cost

Insurance @ 0.5% Capital Cost

Corporate Overhead @ 3% Plant Level Cost

Supervision @ 10% Direct Labor

Payroll Overhead @ 30% Direct Labor

Plant Overhead @ 50% Direct Labor

Labor @ \$4.00/hr

Natural Gas @ \$.60/10^6 Btu

Electricity @ \$.015/KWH

Catalyst: (Estimated Catalyst Life of 15,000 hr)

15% LEL - @ \$1.00/10^3 SCFM of Capacity

25% LEL - @ \$6.00 to \$7.00/10^3 SCFM of Capacity

For convenience of calculation, fuel consumption was calculated on the basis of total adiabatic combustion of fuel, adiabatic system operation, and combustion within the confines of the incinerator only. In practice, fuel consumption can vary up to 30 percent higher than the calculated values, depending upon system design and operating conditions. Partial combustion is also known to occur in the primary heat exchanger if autoignition conditions are approached.

The high value and wide range of catalyst cost is caused by the presence of hexane, which is difficult to burn catalytically at the higher solvent concentration levels investigated. Computer printouts that confirm the larger volume of catalyst needed to convert the hexane are given in Appendix B.

Costs of operation are presented on an annual basis as total cost and cost per 1,000 SCFM processed. Values for 15 percent LEL catalytic and thermal systems are tabulated in Table VI-9. Plots of this information are illustrated in Figures VI-11 and VI-12. In the same manner the values for 25 percent LEL systems are presented in Table VI-10 and Figures VI-13 and VI-14.

Inspection of Tables VI-9 and VI-10 and the graphical presentations in Figures VI-11 through VI-14 leads to the conclusion that operating costs of catalytic

Table VI-9 - Estimated Annual Operating Costs Thermal and Catalytic Incinerators - 15% Lower Explosive Limit

Incinerator Capacity, scfm	1,000	10,000	20,000
Catalytic without Heat Recovery $/yr	8,600	31,500	55,000
$/1000 scfm processed	.0246	.0090	.0079
Catalytic with Primary Heat Recovery, $/yr	10,400	29,800	46,400
$/1000 scfm processed	.0296	.0085	.0066
Catalytic with Primary and Secondary Heat Recovery, $/yr	13,000	31,200	43,000
$/1000 scfm processed	.0372	.0090	.0062
Thermal without Heat Recovery, $/yr	9,800	43,100	78,300
$/1000 scfm processed	.0280	.0123	.0112
Thermal with Primary Heat Recovery, $/yr	10,500	31,600	50,000
$/1000 scfm processed	.0300	.0090	.0070
Thermal with Primary and Secondary Heat Recovery, $/yr	12,300	29,900	42,100
$/1000 scfm processed	.0350	.0085	.0060

Table VI-10 - Estimated Annual Operating Costs Thermal and Catalytic Incinerators - 25% Lower Explosive Limit

Incinerator Capacity, scfm	1,000	10,000	20,000
Catalytic without Heat Recovery $/yr	11,800	74,900	142,000
$/1000 scfm processed	.0337	.0211	.0203
Catalytic with Primary Heat Recovery, $/yr	12,100	68,900	130,000
$/1000 scfm processed	.0344	.0197	.0186
Catalytic with Primary and Secondary Heat Recovery, $/yr	12,900	66,400	122,700
$/1000 scfm processed	.0369	.0190	.0175
Thermal without Heat Recovery $/yr	8,800	39,000	69,000
$/1000 scfm processed	.0292	.0110	.0099
Thermal with Primary Heat Recovery, $/yr	8,500	26,300	42,700
$/1000 scfm processed	.0282	.0075	.0061
Thermal with Primary and Secondary Heat Recovery, $/yr	9,300	23,700	34,800
$/1000 scfm processed	.0330	.0068	.0049

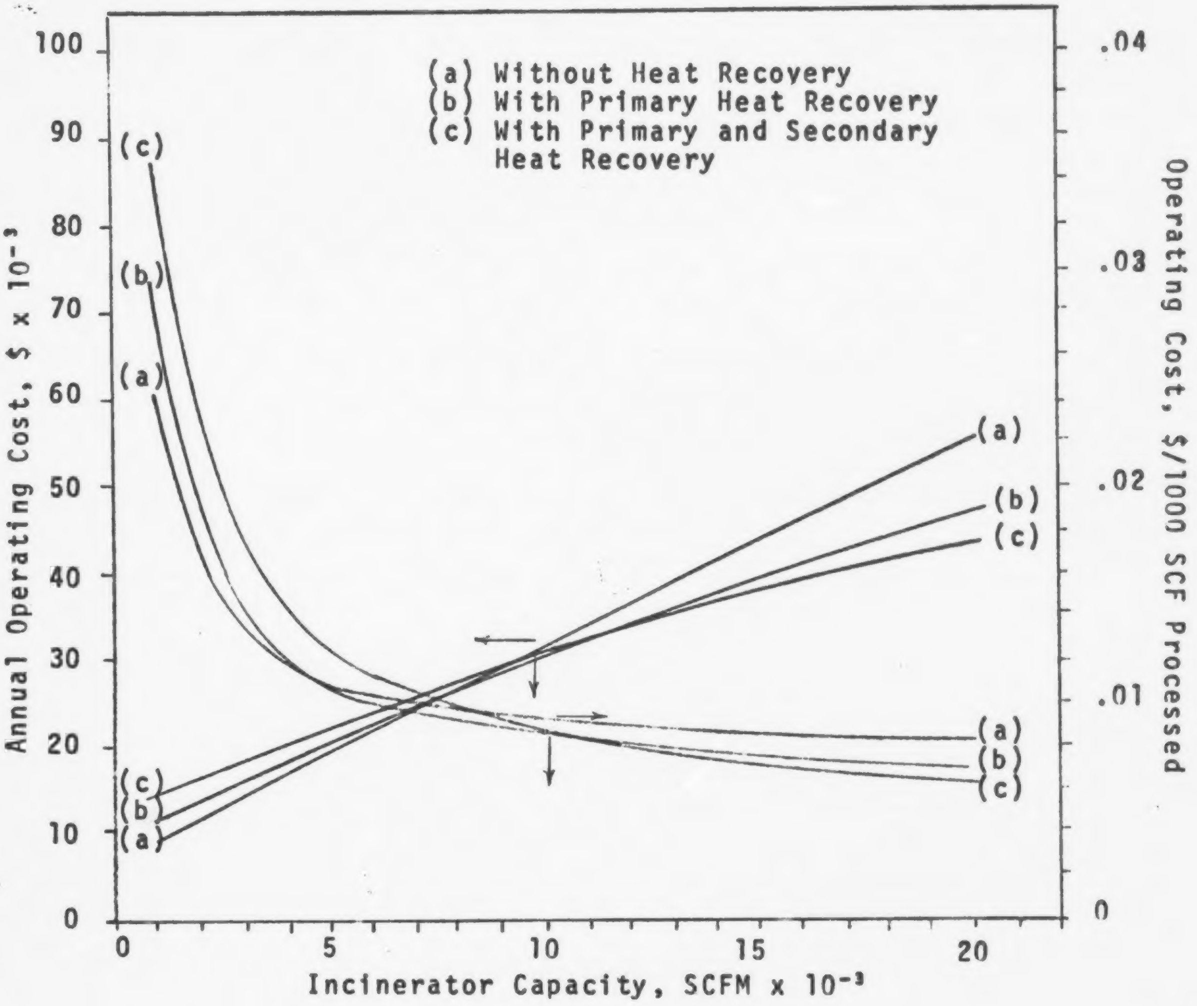

Figure VI-11 - Estimated Catalytic Incinerator Operating Cost-15% LEL (90% Combustion of 50/50 - Hexane/Benzene Mixture @ 15% Lower Explosive Limit)

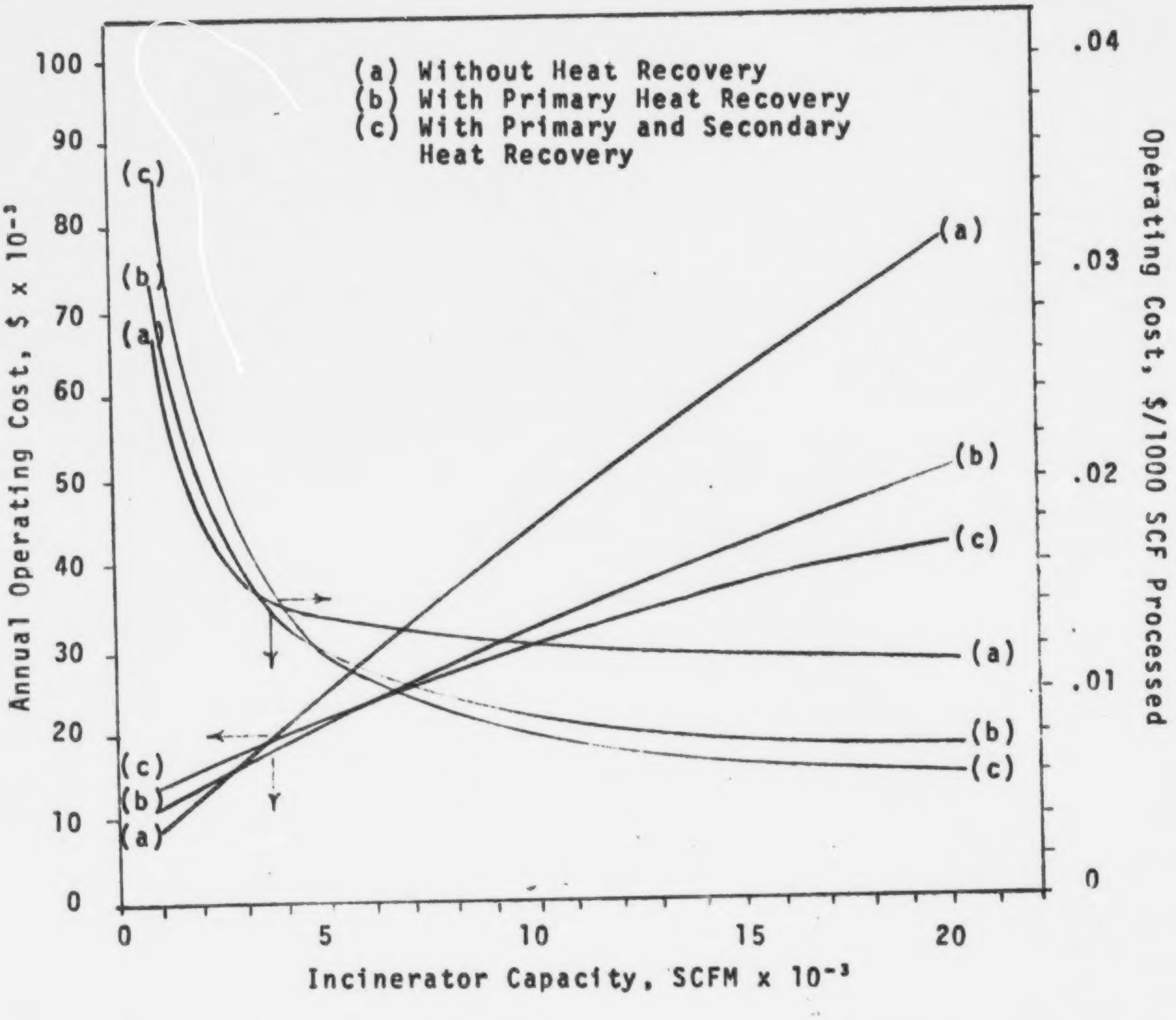

Figure VI-12 - Estimated Thermal Incinerator Operating Cost-15% LEL (90% Combustion of 50/50 - Hexane/Benzene Mixture @ 15% Lower Explosive Limit)

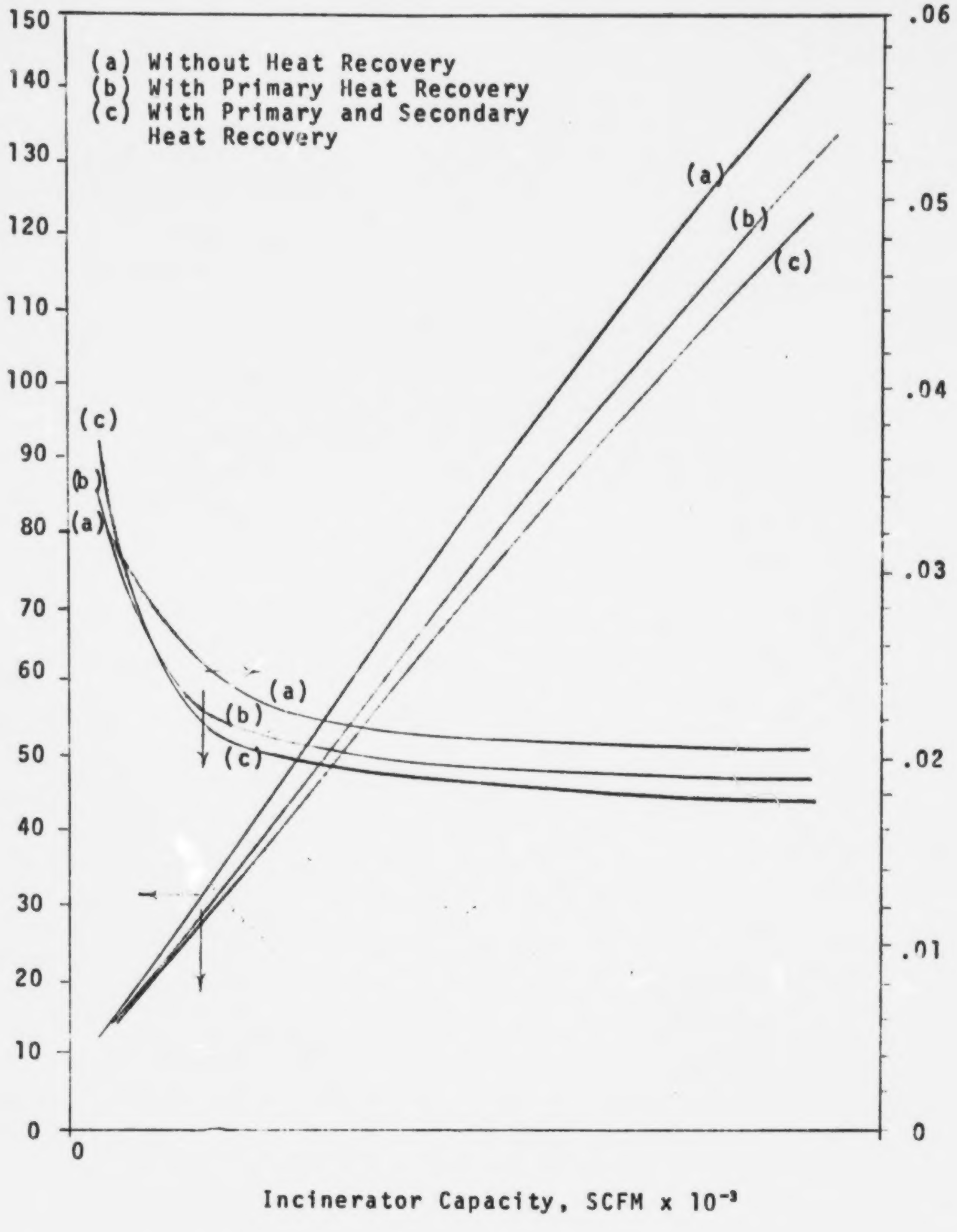

Figure VI-13 - Estimated Catalytic Incinerator Operating Cost (90% Combustion of 50/50 - Hexane/Benzene Mixture @ 25% Lower Explosive Limit)

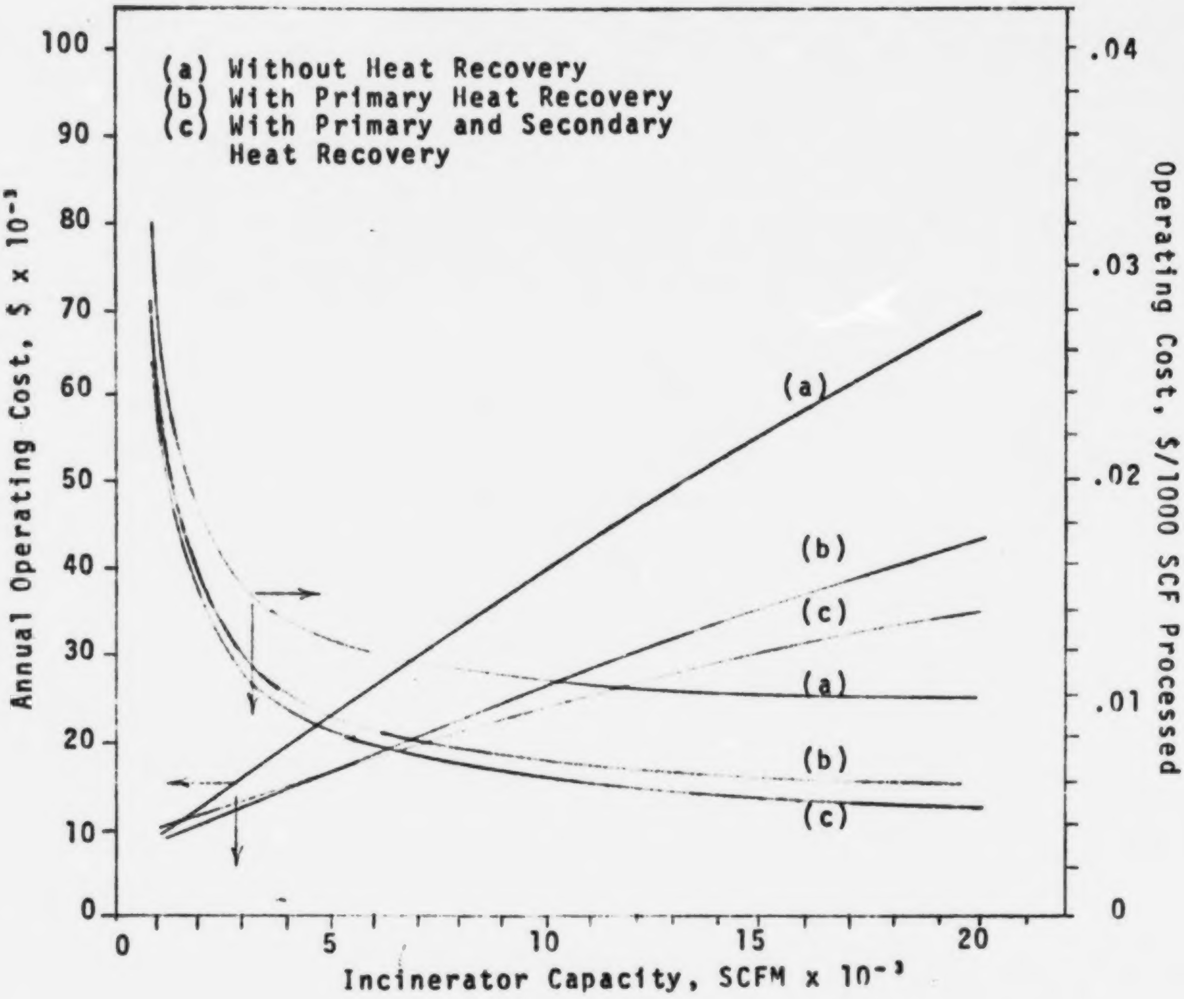

Figure VI-14 - Estimated Thermal Incinerator Operating Cost- 25% LEL (90% Combustion of 50/50 - Hexane/ Benzene Mixture @ 25% Lower Explosive Limit)

systems are considerably higher than those for thermal systems at 25 percent LEL but tend to approach or become lower than costs of thermal systems near 15 percent LEL.

Extrapolation of the data to concentrations below 15 percent LEL justifies this conclusion; costs for all thermal and catalytic systems evaluated appear to reach equivalent operating costs within the range of 13 percent to 18 percent LEL. On this basis, thermal and catalytic units above and below this concentration cost range are preferred as the control method provided incineration is established as the most economical fume abatement process.

The addition of heat recovery equipment in the 15 percent to 25 percent LEL range has a greater effect in reducing the operating costs of thermal than of catalytic incinerators. This is confirmed by data in Figures "I-11 and VI-12 and Figures VI-13 and VI-14. The displacement between the (a) and (b) curves is greater for the thermal units.

Figures VI-11 through VI-14 show further that equivalent operating costs for incinerators with and without heat recovery occur at lower capacities for thermal than for catalytic incinerators. Also, as solvent concentration increases, the incinerator capacity at which the equivalent cost point occurs decreases.

e. Control Method Evaluation - Incineration

Within the scope of this report, the use of incineration as an emission control process is economically justified when a combustible solvent cannot be recovered in a sufficiently uncontaminated condition for reuse in production.

The choice of catalytic or thermal incineration is based on process feasibility and economics.

The presence of catalyst poisons or hydrocarbons that are difficult to convert catalytically usually indicates the use of thermal incineration.

Solvent concentration level in the exhaust air stream is the greatest factor influencing control process economics. Thermal incineration is economically preferred at concentrations above the 13 percent to 18 percent LEL range; catalytic incineration is preferred at concentrations below this range. For systems in which stream concentrations fall within this range, an incineration control method should be selected only after thorough consideration of alternatives.

Addition of heat recovery systems to an incineration process is usually analyzed on the basis of the plant's need for more heat and control process payout.

An incremental analysis of savings versus capital investment and payout is presented for primary and primary with secondary heat recovery systems as applied to the incinerator processes evaluated.

Tables VI-11 and VI-12 present data pertinent to operation at 15 percent and 25 percent LEL exhaust concentrations, respectively. The cost analyses are made by determining differences between total costs (installed and operating) for a given incineration system with and without heat recovery and then calculating a payout after taxes.

The analyses show that payout time for heat recovery is affected by system capacity and hydrocarbon concentration of these factors increase. Payout time for heat recovery is also reduced as incinerator operating temperature increases, because the higher thermal driving force lessens heat exchanger costs. The shorter payout time of thermal versus catalytic systems illustrates this point.

4. Adsorption

Control of hydrocarbon emissions by adsorption on activated carbon is generally applied when recovery of adsorbed material is economically desirable. Other applications are for control of very low concentrations of noxious organics not readily handled by catalytic incineration and for collecting and concentrating low-concentration emissions for subsequent disposal by incineration.

a. General Case Description

For convenience of calculation and to allow comparison with thermal and catalytic incineration systems, the adsorption systems studies were based on the same emission source: a paint bake oven exhausting benzene/hexane in air at 375°F.

Table VI-11 - Differential Savings Versus Differential Capital Investment and Payout

15% Lower Explosive Limit - (Base Case - Incinerators Without Heat Recovery)

Incinerator Capacity, scfm	1,000	10,000	20,000
Catalytic with Primary Heat Recovery vs Catalytic without Heat Recovery			
Differential Installed Cap. Cost, $	17,300	60,900	91,300
Differential Gross Savings (Loss), $	(1,800)	1,700	8,600
Differential Tax @ 50%, $	-	850	4,300
Differential Net Savings (After Tax),$	-	850	4,300
Payout Cap. Investment, Jr.	-	8.8	6.8
Catalytic with Primary and Secondary Heat Recovery vs Catalytic without Heat Recovery			
Differential Installed Cap. Cost, $	38,400	136,000	204,000
Differential Gross Savings (Loss), $	(4,400)	300	12,000
Differential Tax @ 50%, $	-	150	6,000
Differential Net Savings (After Tax), $	-	150	6,000
Payout Cap. Investment, Yr.	-	9.9	7.7
Thermal with Primary Heat Recovery vs Thermal without Heat Recovery			
Differential Installed Cap. Cost, $	17,300	60,900	91,300
Differential Gross Savings (Loss), $	(700)	11,500	28,300)
Differential Tax @ 50%	-	5,750	14,150
Differential Net Savings (After Tax), $	-	5,750	1[illegible].50
Payout Cap. Investment, Yr.	-	5.1	3.9

Table VI-11 (Continued)

Incinerator Capacity, scfm	1,000	10,000	20,000
Thermal with Primary and Secondary Heat Recovery vs Thermal without Heat Recovery			
Differential Installed Cap. Cost, $	33,300	117,700	117,600
Differential Gross Savings (Loss), $	(2,500)	13,200	36,200
Differential Tax @ 50%, $	-	6,600	18,100
Differential Net Savings (After Tax),$	-	6,600	18,100
Payout Cap. Investment, Yr.	-	6.4	3.9

Table IV-12 - Differential Savings Vs Differential Capital Investment and Payout

25% Lower Explosive Limit - (Base Case - Incinerators Without Heat Recovery)

Incinerator Capacity, scfm	1,000	10,000	20,000
Catalytic with Primary Heat Recovery vs Catalytic without Heat Recovery			
Differential Installed Cap. Cost, $	7,900	25,400	51,700
Differential Gross Savings (Loss), $	(300)	6,000	12,000
Differential Tax @ 50%, $	-	3,000	6,000
Differential Net Savings (After Tax),$	-	3,000	6,000
Payout Cap. Investment, Yr.	-	4.6	4.6
Catalytic with Primary and Secondary Heat Recovery vs Catalytic without Heat Recovery			
Differential Installed Cap. Cost, $	18,500	67,000	120,800
Differential Gross Savings (Loss), $	(1,100)	8,500	19,300
Differential Tax @ 50%, $	-	4,250	9,650
Differential Net Savings (After Tax),$	-	4,250	9,650
Payout Cap. Investment, Yr.	-	6.1	5.6
Thermal with Primary Heat Recovery vs Thermal without Heat Recovery			
Differential Installed Cap. Cost, $	9,800	38,600	71,100
Differential Gross Savings (Loss), $	300	12,700	26,300
Differential Tax @ 50%, $	150	6,350	13,150
Differential Net Savings (After Tax), $	150	6,350	13,150
Payout Cap. Investment, Yr.	8.7	3.8	3.5

Table VI-12 (Continued)

Incinerator Capacity, scfm	1,000	10,000	20,000
Thermal with Primary and Secondary Heat Recovery vs Thermal without Heat Recovery			
Differential Installed Cap. Cost, $	20,300	80,200	138,100
Differential Gross Savings (Loss), $	(500)	15,300	34,200
Differential Tax @ 50%, $	-	7,650	17,100
Differential Net Savings (After Tax),$	-	7,650	17,100
Payout Cap. Investment, Yr.	-	5.1	4.5

Three base cases were evaluated: adsorption with solvent recovery; adsorption with incineration and no heat recovery; and adsorption with incineration plus heat recovery.

b. Adsorption With Solvent Recovery

Adsorption is achieved by passing cool, particulate-free and hydrocarbon-laden exhaust gases through a bed of activated carbon. As required, the gases are filtered or scrubbed to avoid fouling the adsorbent with dust and then cooled to approximately 100°F to increase the driving force in the transfer process.

This section of the study evaluated dual horizontal fixed-bed adsorption systems with capacities of 1,000 SCFM and 20,000 SCFM processing 25 percent LEL concentrations of 50/50 benzene-hexane vapor mixtures (equivalent to about 0.3 percent by volume). A working capacity equal to 50 percent of saturation capacity or 0.1 pound adsorbate per pound adsorbent was assumed in determining cycle times and utility requirements. This value is based on dynamic column tests performed by a vendor and on the adsorption isotherms for benzene and hexane. The dynamic column test indicates preferential adsorption of hexane.

Bed dimensions and carbon charge were determined by the adsorption system vendor. An emission reduction value of 90 percent across the carbon bed was used in the analysis. Steam regeneration was held constant at 3 pounds of steam per pound of solvent. Condensation, subcooling, and decantation recovery were employed in operating cost computations. Distillation was not considered, since the purity of decanted solvent was assumed to be adequate for recycle to the coating process. The process flow sequence is shown in Figure VI-15. The process consists of filtering and then cooling oven gases from 375°F to 100°F, passing the stream through one of the beds to adsorb solvent vapors, and venting the clean gases to the atmosphere. The remaining bed is simultaneously regenerated with low pressure steam. The resultant vapors are condensed at 212°F and subcooled to 100°F. Separation of the solvent-water condensate is accomplished by decantation.

c. Adsorption With Incineration - No Heat Recovery - No Solvent Recovery

The process consisted of a dual-bed adsorption system, a booster fan, and a thermal incinerator.

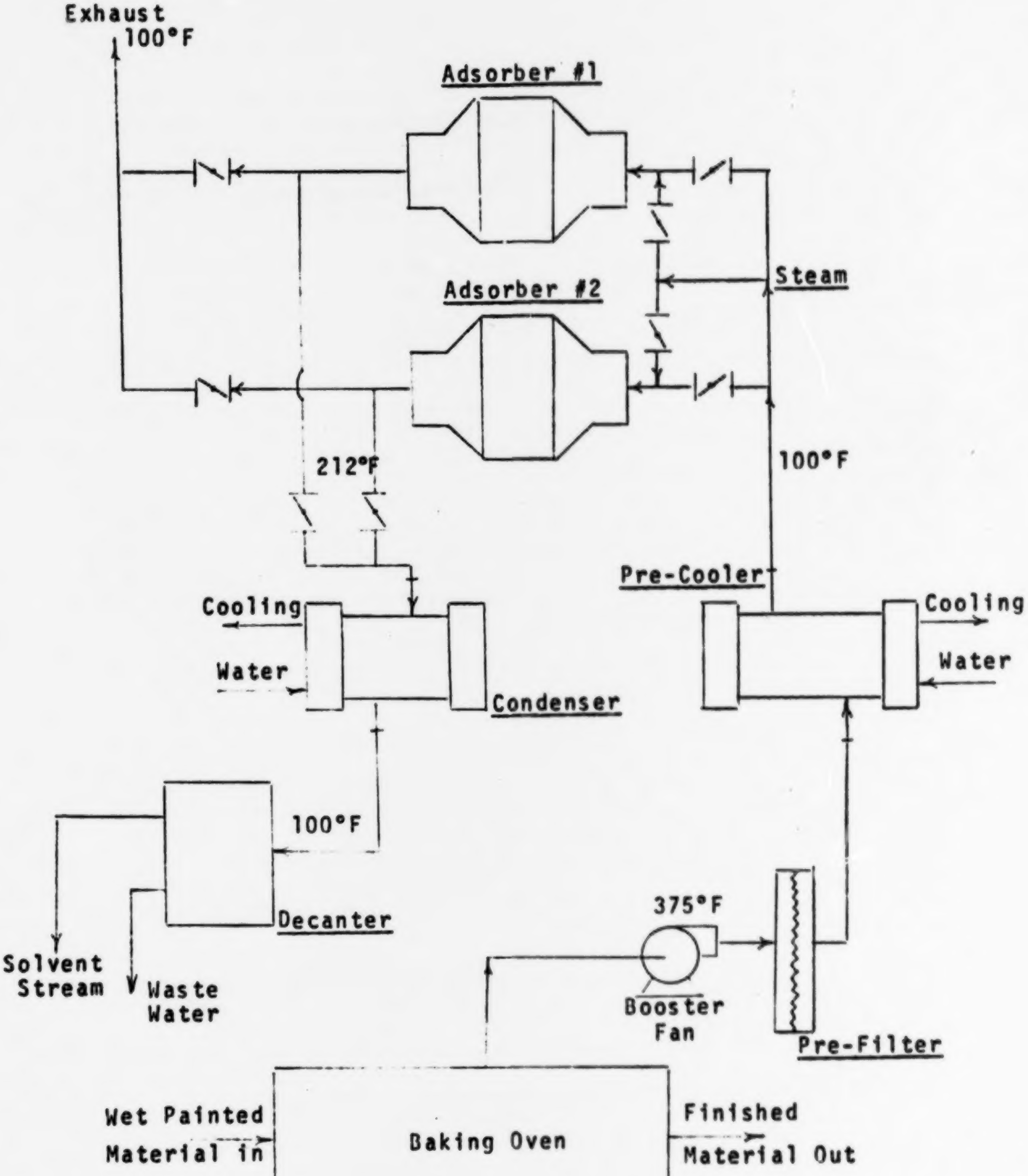

Figure VI-15 - Adsorption With Solvent Recovery-Flow Sheet

The process flow diagram for this scheme is presented in Figure VI-16. The stream temperatures shown are common to both oven exhaust concentrations considered. The stripped oven exhaust gases are vented to the atmosphere. The solvent-laden stream from the regeneration cycle is fed to the incinerator.

Oven exhaust rates of 1,000 SCFM, 10,000 SCFM, and 20,000 SCFM with hexane-benzene solvent concentration levels at 200 ppm and 25 percent LEL were incorporated in the system analysis. At the 200 ppm concentration, the adsorber carbon charge was reduced to the minimum amount for each SCFM capacity level, while incinerator capacity was reduced to and fixed at 500 SCFM for all oven volume capacity levels. This was done because the 500 SCFM incinerator appeared to be the smallest size unit readily available from vendors and the closest to meeting process requirements. At the 25 percent LEL concentration, the maximum carbon charge for each adsorber was utilized. Incinerator capacity was based on adsorber regeneration rate plus the amount of combustion air needed to maintain a 1450°F stack temperature. The extremes in concentration were chosen to illustrate areas suited to application of this process.

d. Adsorption With Incineration and Heat Recovery

The schemes covered under this section are a continuation of the process shown in Figure VI-16 and described under "Adsorption with Incineration - No Heat Recovery - No Solvent Recovery". The additions of primary, and primary with secondary, heat recovery to the thermal incinerators are shown in Figures VI-17 and VI-18, respectively. The same thermal efficiencies used to evaluate heat recovery for the incineration schemes were incorporated in this phase of the study (see p. 34).

Systems were again evaluated at capacities of 1,000 SCFM, 10,000 SCFM, and 20,000 SCFM and a 25 percent LEL hexane-benzene concentration. In each case, incinerator size was determined by the quantity of air required to mix with the regenerated adsorber stream and maintain the incinerator outlet temperature at 1450°F.

e. Installed Capital Cost - Adsorption

Installed capital costs of the adsorption-solvent recovery systems were based on one vendor's quotation, which

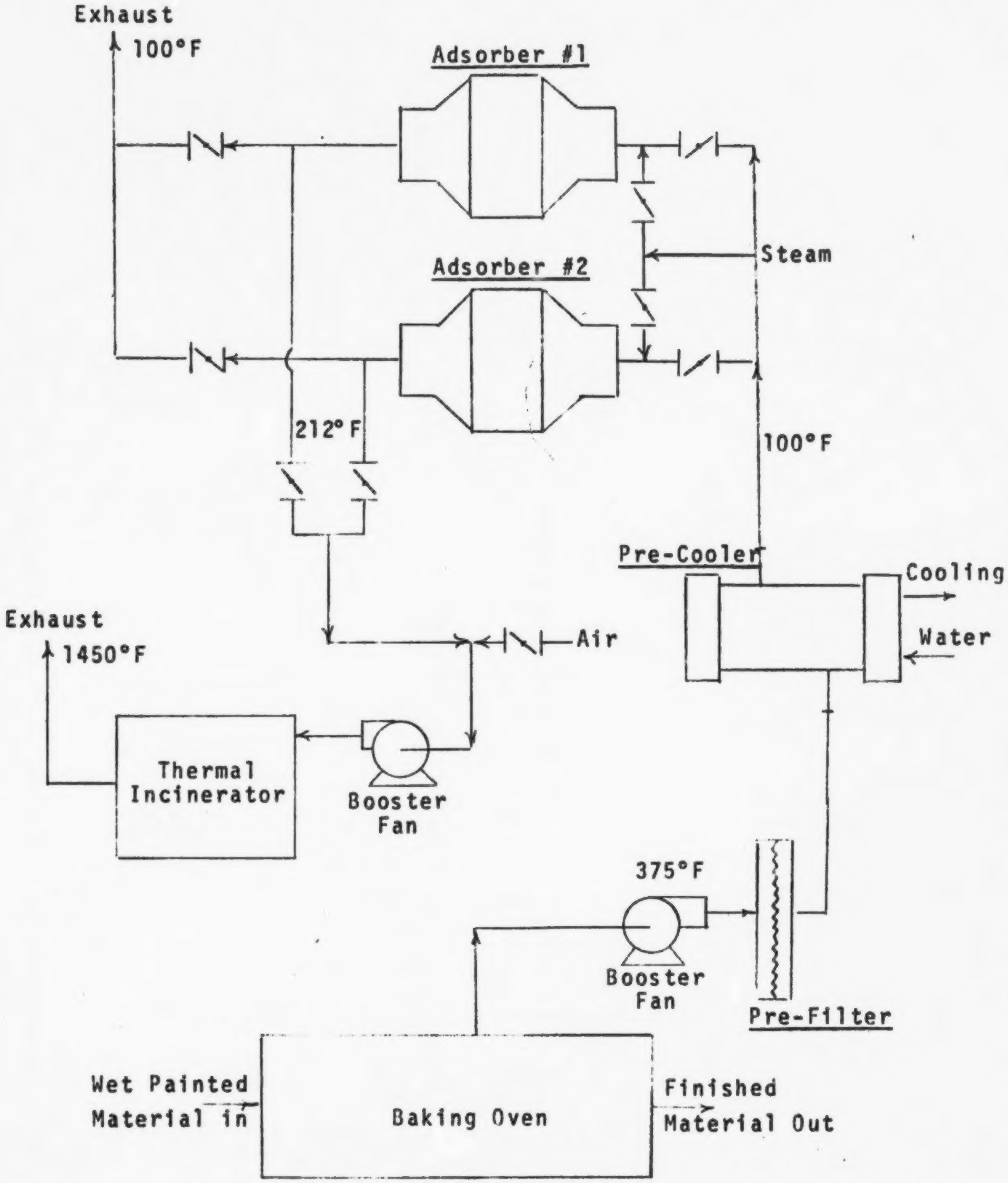

Figure VI-16 - Adsorption With Thermal Incineration - No Heat Recovery - Flow Sheet

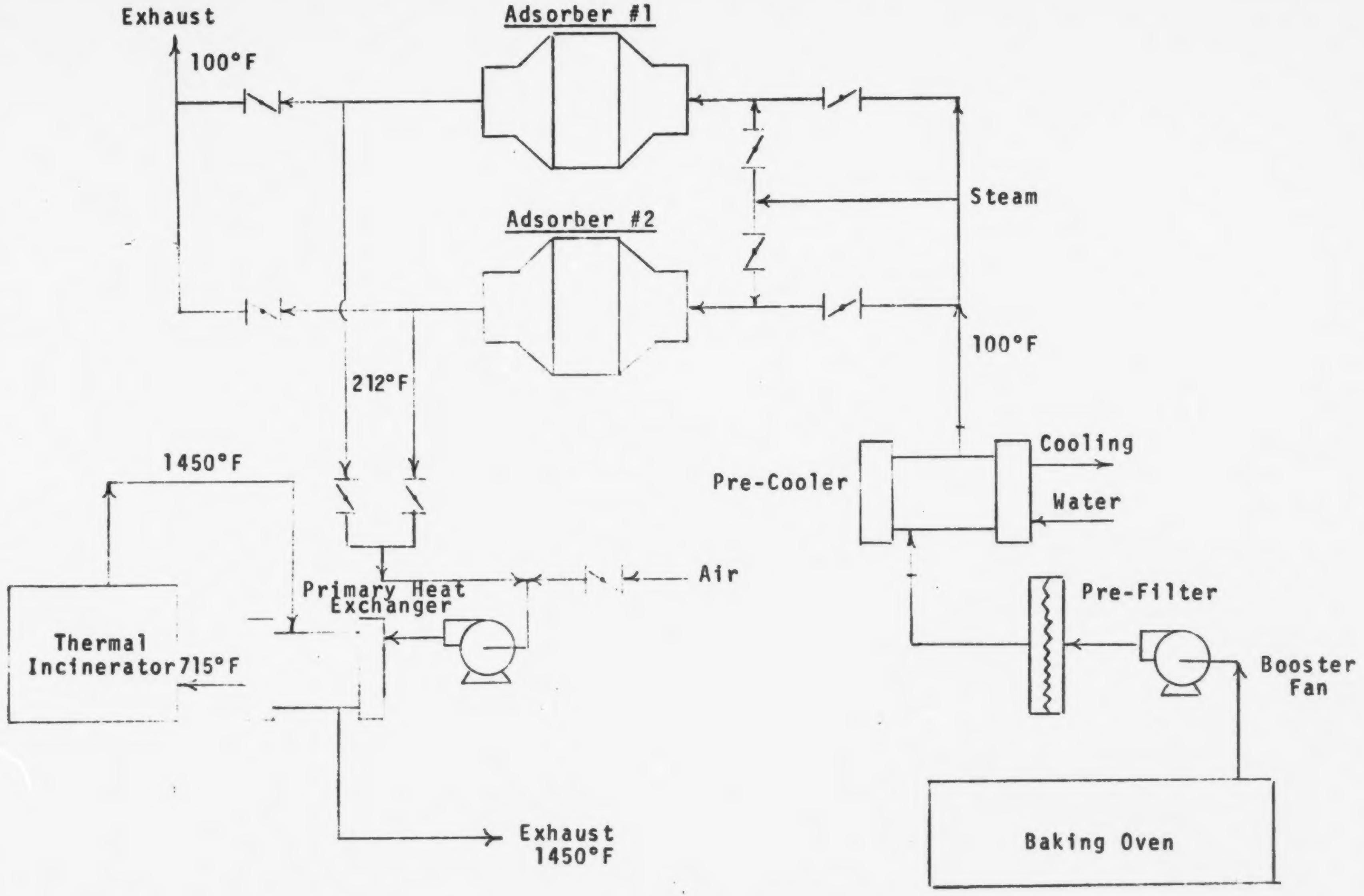

Figure VI-17 - Adsorption With Thermal Incineration/Primary Heat Recovery - Flow Sheet

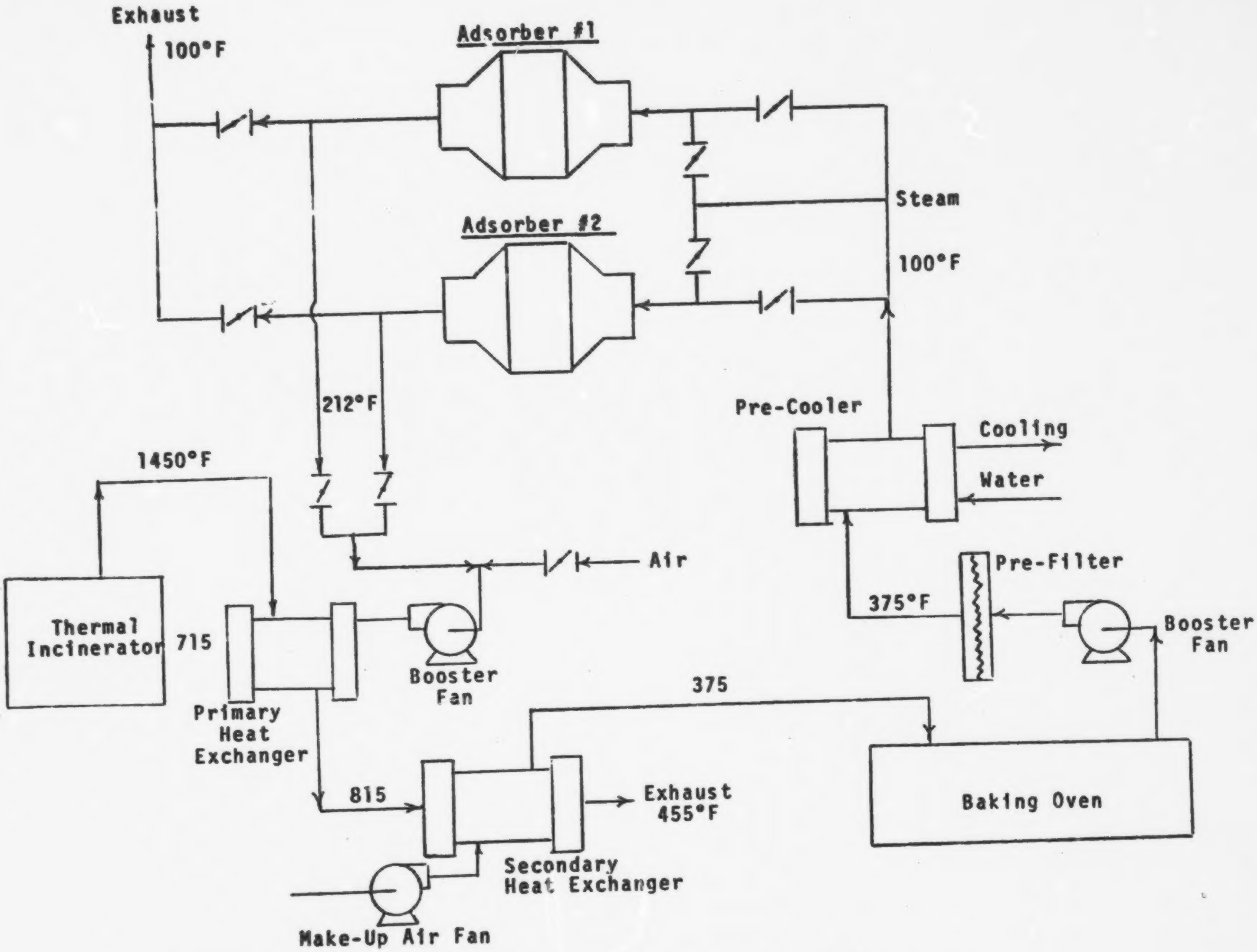

Figure VI-18 - Adsorption With Thermal Incineration/Primary and Secondary Heat Recovery

itemized the equipment and installation costs for the package units. The quotation is shown in Appendix C. Additional prices for the precooler and prefilter, not included in vendor's package, were obtained by verbal quotations and through use of correlations.

Installed capital costs of adsorption-thermal incineration systems without and with heat recovery were based on previously discussed quotations for the adsorbers and incinerators.

Installed costs are tabulated in Table VI-13 and shown graphically in Figure VI-19; a detailed presentation is given on construction cost estimate sheets in Appendix C. Adsorption with solvent recovery shows the lowest installed price of the adsorption systems investigated at 25 percent LEL concentration. Installed costs increase, in order, for the systems of adsorption-incineration without heat recovery, adsorption-incineration with primary heat recovery, and adsorption-incineration with primary and secondary heat recovery.

For the adsorption-incineration system used to process exhaust streams at the 200 ppm level, the installed adsorption-solvent recovery system and the adsorption-incineration no heat recovery system at 25 percent LEL.

When compared on the basis of equivalent heat recovery schemes, the cost curves of Figure VI-19 lie between those for thermal and catalytic incineration, shown in Figure VI-10.

f. Operating Cost - Adsorption

Operating costs for adsorption-solvent recovery and adsorption-thermal incineration systems are shown on the manufacturing estimate sheets in Appendix C. Values were calculated for all systems at the 25 percent LEL level and in addition for the adsorption-incineration, no heat recovery system at the 200 ppm level. Costs were determined by employing the following rates and percentages:

Operating	- 2 shifts/day, 365 days, 0.5 man hours direct labor per shift
Maintenance	@ 5% Capital Cost

Table VI-13 - Estimated Installed Costs of Adsorption Systems

Adsorber Capacity scfm	1,000	10,000	20,000
25% Lower Explosive Limit			
With Solvent Recovery, $	54,700	120,300	207,300
With Thermal Incineration/No Heat Recovery, $	66,800	150,700	256,600
With Thermal Incineration/ Primary Heat Recovery, %	75,800	190,300	321,300
With Thermal Incineration/ Primary & Secondary Heat Recovery, $	88,800	239,900	398,500
200 ppm			
With Thermal Incineration/No Heat Recovery, %	66,800	130,200	241,900

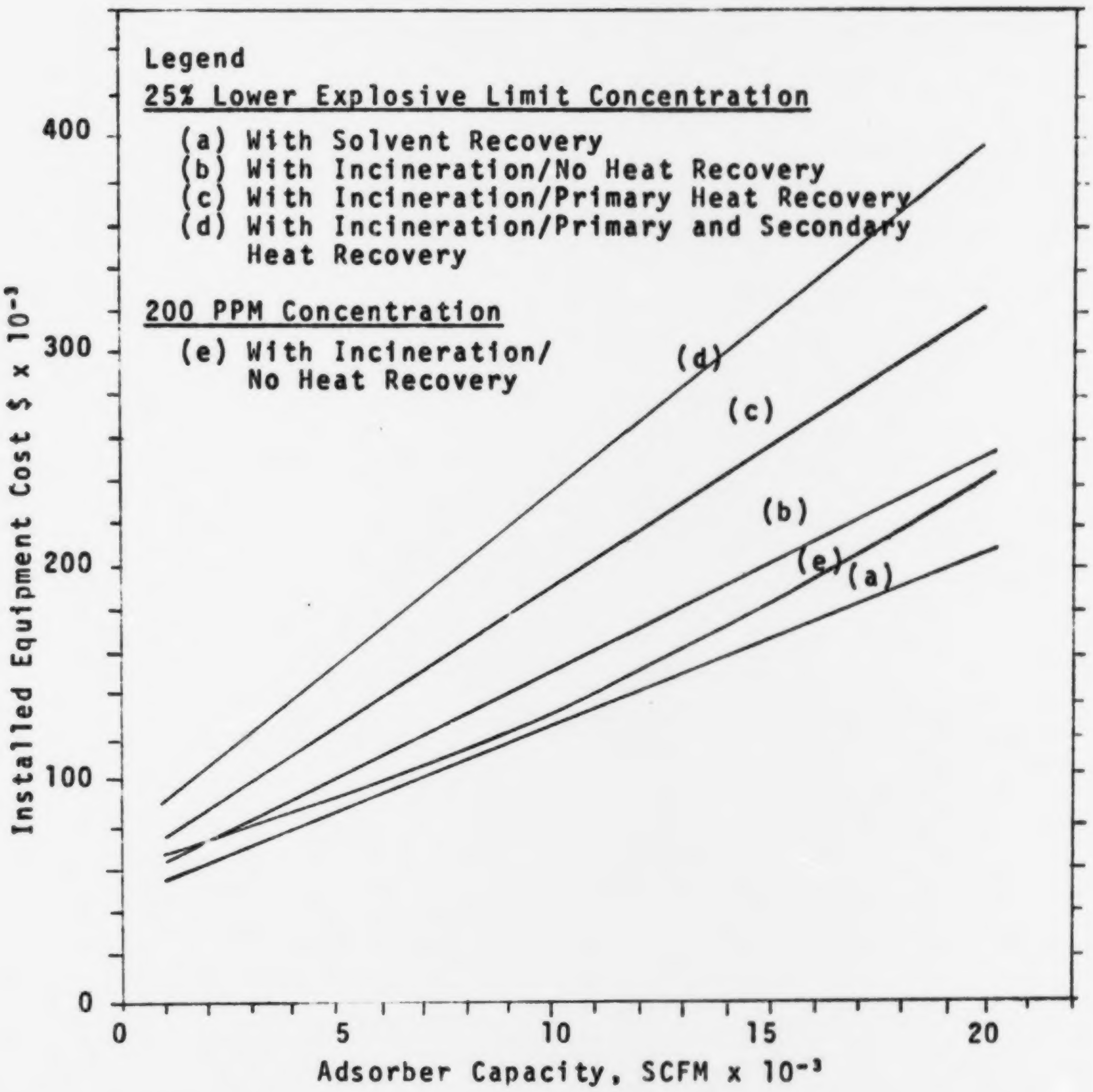

Figure VI-19 - Estimated Installed Adsorption System Cost (90% Combustion or Recovery of 50/50-Hexane/Benzene Mixture)

Depreciation	@ 10% Capital Cost
Property Taxes	@ 1% Capital Cost
Insurance	@ 0.5% Capital Cost
Corporate Overhead	@ 3% Plant Level Cost
Supervision	@ 10% Direct Labor
Payroll Overhead	@ 30% Direct Labor
Plant Overhead	@ 50% Direct Labor
Labor	@ $4.00/hr
Cooling Water	- $.03/1,000 gal.
Steam	- $1.00/1,000 gal.
Electricity	- $.015/KWH
Activated Carbon	- $.50/lb, 5 yr service life

This list is the same as that used for the incineration evaluation, except that prices for additional utilities and different operating materials are included. The values of recovered solvents were taken at $.03 per pound for benzene and $.0375 per pound for hexane. Adiabatic system operation was assumed in computing utility consumption; these utility calculations are included in Appendix C.

A summary of annual operating costs is presented in Table VI-14 and Figure VI-20 as total dollars and dollars per 1,000 SCF processed.

These data show that adsorption with solvent recovery is the most economical process considered at the 25 percent LEL level. A savings with this process is apparent for the hexane-benzene system at capacities in excess of 5,000 SCFM. The savings rate appears to level off at $.005/1,000 SCF processed between 15,000 and 20,000 SCFM capacity values.

Operating costs become higher for the adsorption-incineration and adsorption-incineration-heat recovery systems in that order. This trend is generally in line with that shown for the installed costs of these systems.

Table VI-14 - Estimated Annual Operating Costs of Adsorption Systems

Adsorber Capacity, scfm	1,000	10,000	20,000
25% Lower Explosive Limit			
With Solvent Recovery, $/yr	9,500	9,500*	30,700*
$/1000 scf Processed	.0270	.0027*	.0044*
With Thermal Incineration/No Heat Recovery, $/yr	17,100	51,500	89,300
$/1000 scf Processed	.0490	.0147	.0128
With Thermal Incineration/ Primary Heat Recovery, $/yr	18,700	59,400	140,700
$/1000 scf Processed	.0540	.0170	.0150
With Thermal Incineration/Primary & Secondary Heat Recovery, $/yr	19,900	58,200	96,600
$/1000 scf Processed	.0662	.0166	.0138
200 ppm			
With Thermal Incineration/No Heat Recovery, $/yr	15,900	36,600	65,000
$/1000 scf Processed	.0453	.0100	.0093

*Indicates a savings as opposed to operating cost

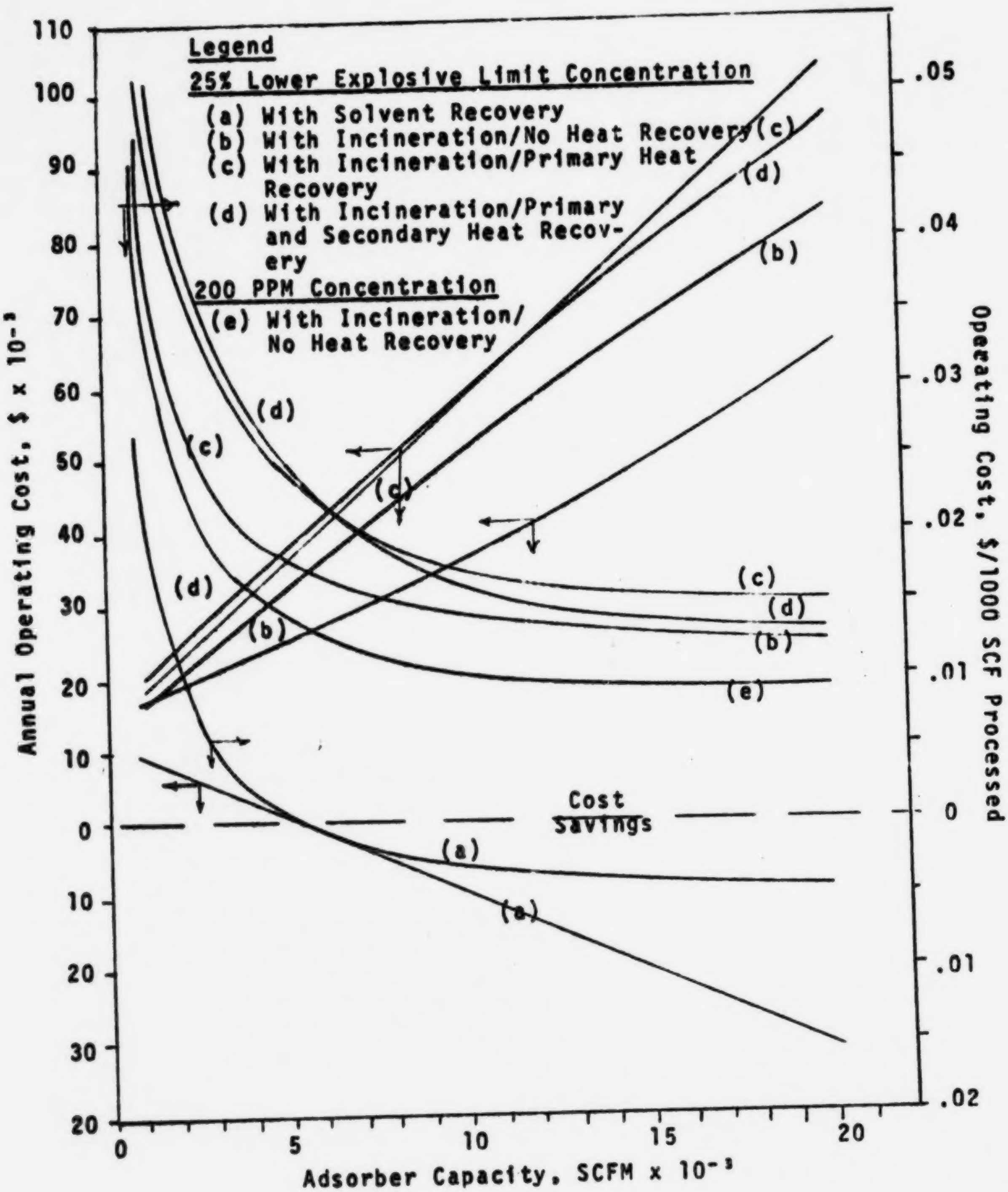

Figure VI-20 - Adsorption Systems Estimated Operating Cost (90% Combustion or Recovery of 50/50 - Hexane/Benzene Mixture)

The operating cost for the adsorption and incineration with no heat recovery decreases as concentration is reduced from 25 percent LEL to 200 ppm. This cost decrease is caused by decreases in the size of the carbon bed, number of regeneration cycles, and consumption of utilities. The cost decrease is further accented as capacity increases.

g. Control Method Evaluation-Adsorption

The process of activated carbon adsorption with solvent recovery should be used for emission control in plants where the recovered solvent is free enough, or can feasibly be made free enough, of contaminants to be reused in the process. This is the most economical of the control systems evaluated.

Results of computing savings versus capital investment and payout for the 25 percent LEL benzene-hexane system are summarized in Table VI-15. Review of Table VI-15 in conjunction with curve (a) of Figure VI-20 demonstrates that this process begins to show a payout at capacities greater than 5,000 SCFM. At capacities in excess of 20,000 SCFM, this process is economically attractive regardless of emission control considerations.

Processes employing adsorption with incineration cannot be justified on economic grounds under any conditions that allow normal incinerator operations. Adsorption-incineration without heat recovery does appear to be attractive for disposal of very low concentration effluents (<500 ppm) that cannot be controlled by catalytic incineration (eg. effluents that contain catalytic poisons).

Evaluation of the adsorption-incineration process at 200 ppm was included to illustrate costs associated with this application. For this example, the low concentration effluent was assumed to be contaminated by a catalyst poison, thus eliminating catalytic incineration. Also, at this low concentration, direct flame incineration is not economically feasible because of the high supplemental fuel costs. Therefore, solvent must be collected or in effect concentrated for destruction by thermal methods. The basis for choosing this type of system is one of control process feasibility and economics.

Table VI-15 - Savings vs Capital Investment and Payout for Adsorption/Solvent Recovery - 25% Lower Explosive Limit

Adsorber Capacity, scfm	1,000	10,000	20,000
Installed Capital Cost, $	54,700	120,300	207,300
Savings (Loss) Before Taxes, $	(9,500)	9,500	30,700
Tax @ 50%, $	-	4,750	15,350
Savings (Loss) After Taxes, $	(9,460)	4,750	15,350
Payout on Investment, yr	-	7.2	5.7

5. Wet Scrubbing

a. General

In Section B of this chapter, wet scrubbing methods were identified as suitable for control of emissions containing organic particulates, aerosols, and soluble gases. To illustrate the economic variables involved in application of scrubbing techniques, two industrial applications were evaluated. The actual design capacity ranges were extrapolated to show the effects of variation of exhaust gas flow rates on the capital and operating costs.

b. Process Description - Incineration/Scrubbing

The control process shown on the flow sheet of Figure VI-21 is designed to dispose of a 5 percent by weight solution of DDT in kerosene.

The operational sequence is comprised of collecting waste liquid in the holding tank, pumping the liquid to the incinerator, where plant air is provided for atomization of the mixture, and burning the mixture at 1600°F after blending it with 20 percent excess combustion air supplied by the blower. The hot gases are sent to the packed absorption tower, where the gases are adiabatically cooled and hydrogen chloride is absorbed with water. The cleaned and cooled gases then pass out through the stack to the atmosphere.

This evaluation is based on the assumption that the waste stream will be an intermittent flow of varying magnitude, which is contingent on upstream production requirements. A two-shift operating schedule was selected for the emission control process; this schedule does not necessarily coincide with that of the main process and was selected to keep manpower requirements at a minimum. The additional control process capacity realized by basing the evaluation on this premise provides for future plant expansion and operating flexibility.

A more detailed description of the installation is provided in Appendix D. Although the calculations and economic evaluation are based solely on the absorption of the HCl component of the incinerator exhaust stream, trace organics, either as particulates or soluble gases would also be collected.

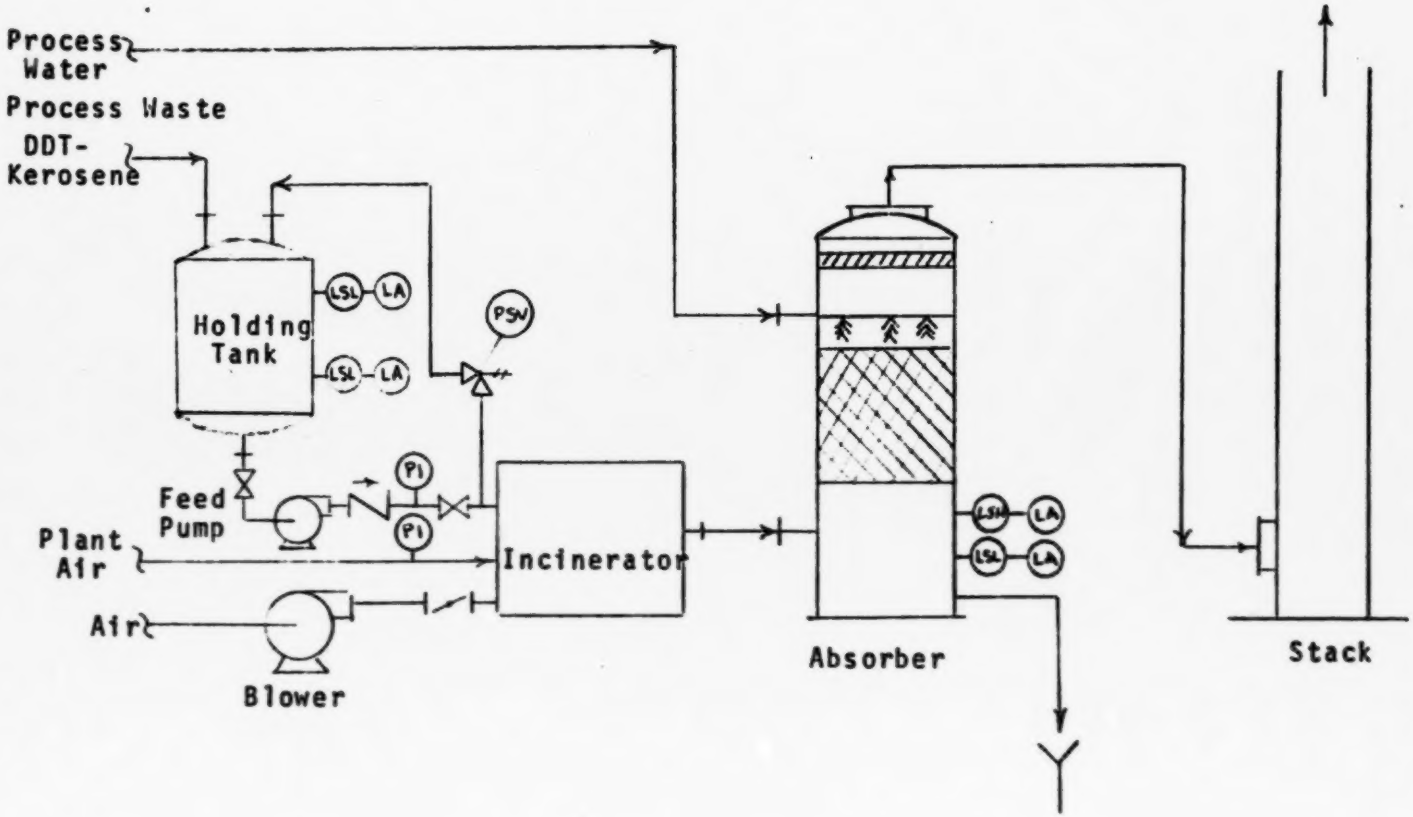

Figure VI-21 - Incineration/Absorption - Process Flow Sheet (Kerosene & DDT)

The major incinerator combustion products calculated for the feed and operating conditions are as follows:

Components	Mol %
CO_2	16.5948
N_2	78.2904
O_2	3.4679
NO	0.0131
OH	0.0001
Cl_2	0.0012
HCl	0.1448
H_2O	1.4874
	99.9997

c. Process Description Scrubbing/Absorption

This scheme is shown diagramatically in Figure VI-22. The plant operates 11 reactors for the manufacture of specialty organic chemicals. The formulations are made batchwise. The steps consist of feeding the raw materials to the reactor and mixing them under a heated and/or cooled reactor jacket.

Each reactor exhaust line is provided with a valve ahead of its connection to the scrubber system feed duct. Since only some reactors are on stream at a given time, the individual valving provides for more efficient operation.

The exhaust gases pass through a venturi scrubber, where entrained solids are knocked out by the recirculating water. The venturi scrubber is physically close-coupled to the packed tower. The water-soluble vapors are removed in the absorber. Scrubbed gases then pass out of the packed tower through the fan, and thence to a stack.

Water is recirculated from the bottom of the column, and split between the venturi scrubber and the spray nozzles in the column. A portion of the water is

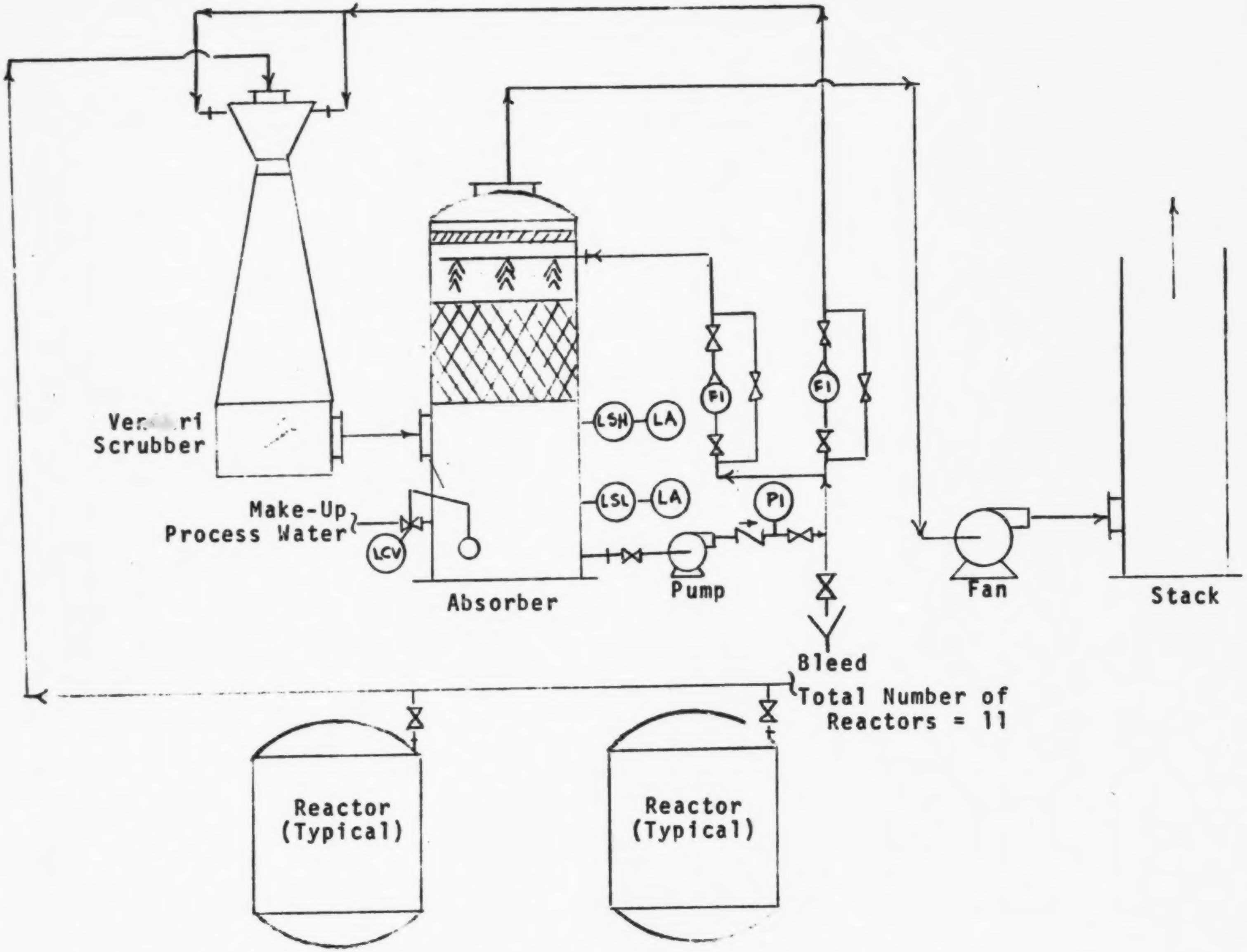

Figure VI-22 - Scrubbing/Absorption - Process Flow Sheet

bled off. Fresh makeup water is brought in automatically to maintain the level in the bottom of the absorber.

Production incorporates a large number of raw materials, including organic and inorganic compounds in both liquid and in solid forms. Solids are charged manually to the reactors via a chute through the manhole. Liquids are charged to the reactors from drums and bulk storage tanks. Transfer from drums is accomplished with portable pumps and hoses Because of the significant quantities involved, bulk liquids are charged by pumping directly from storage.

The venturi scrubber is designed to reduce solids loading of the stack discharge to less than .01 grain/cubic foot.

A variety of gaseous compounds are exhausted to the scrubbing system. Most of the liquid chemicals are used in small quantities and have relatively low vapor pressures. Because isopropanol exhibits the highest vapor pressure of the raw materials used in production, it is the contaminant upon which the absorber design is based. The design data for the absorber are as follows:

Gas Rate - 642 lb-mol/hr (4000 SCFM)

Liquid Rate - 1400 lb-mol/hr

Mol Fraction Isopropanol in Gas Inlet - 0.1

Mol Fraction Isopropanol in Gas Outlet - 0.0073

Tower Diameter - 4 ft.

Packed Height of Tower - 6 ft.

Packing - 1" Ceramic Intalox Saddles

Height of a Transfer Unit - 1.5 ft.

Number of Transfer Units - 4

d. Installed Cost - Incineration/Absorption

Process equipment costs were based on the 100 GPH DDT - kerosene waste stream case illustrated in Appendix E. Equipment costs for the 500 GPH systems were determined through use of the six-tenths factor rule; an exception was the capital costs of the direct flame incinerator which were obtained from a correlation developed from one vendor's budget quote.

The incinerator cost correlation is shown in Appendix D, where incinerator exhaust rates of 2000 SCFM, 10,000 SCFM, and 20,000 SCFM are shown to be equal to waste stream flow rates of 100 GPH, 500 GPH, and 1000 GPH.

Cost for installation of equipment was estimated at 100 percent of purchased equipment cost.

These costs are summarized in Table VI-16 and shown graphically in Figure VII-23; they are detailed on construction estimate sheets in Appendix D.

Table VI-16 - Estimated Installed Costs of Incinerator/ Absorber Systems (Kerosene and DDT Waste)

System Capacity, SCFM (Based on Absorber Feed Rate)	2000	10,000	20,000
Installed Capital Cost, $	60,000	136,000	202,000

e. Operating Costs - Incineration/Absorption

Operating costs for the incineration/absorption control processes are developed on manufacturing estimate sheets in Appendix D. The values were calculated through use of the following percentages and rates:

Operating - 2 shifts/day, 330 days/year

Maintenance @ 5% Capital Cost

Depreciation @ 10% Capital Cost

Property Taxes @ 1% Capital Cost

Insurance @ 0.5% Capital Cost

Corporate Overhead @ 3% Plant Level Cost

Supervision @ 10% Direct Labor

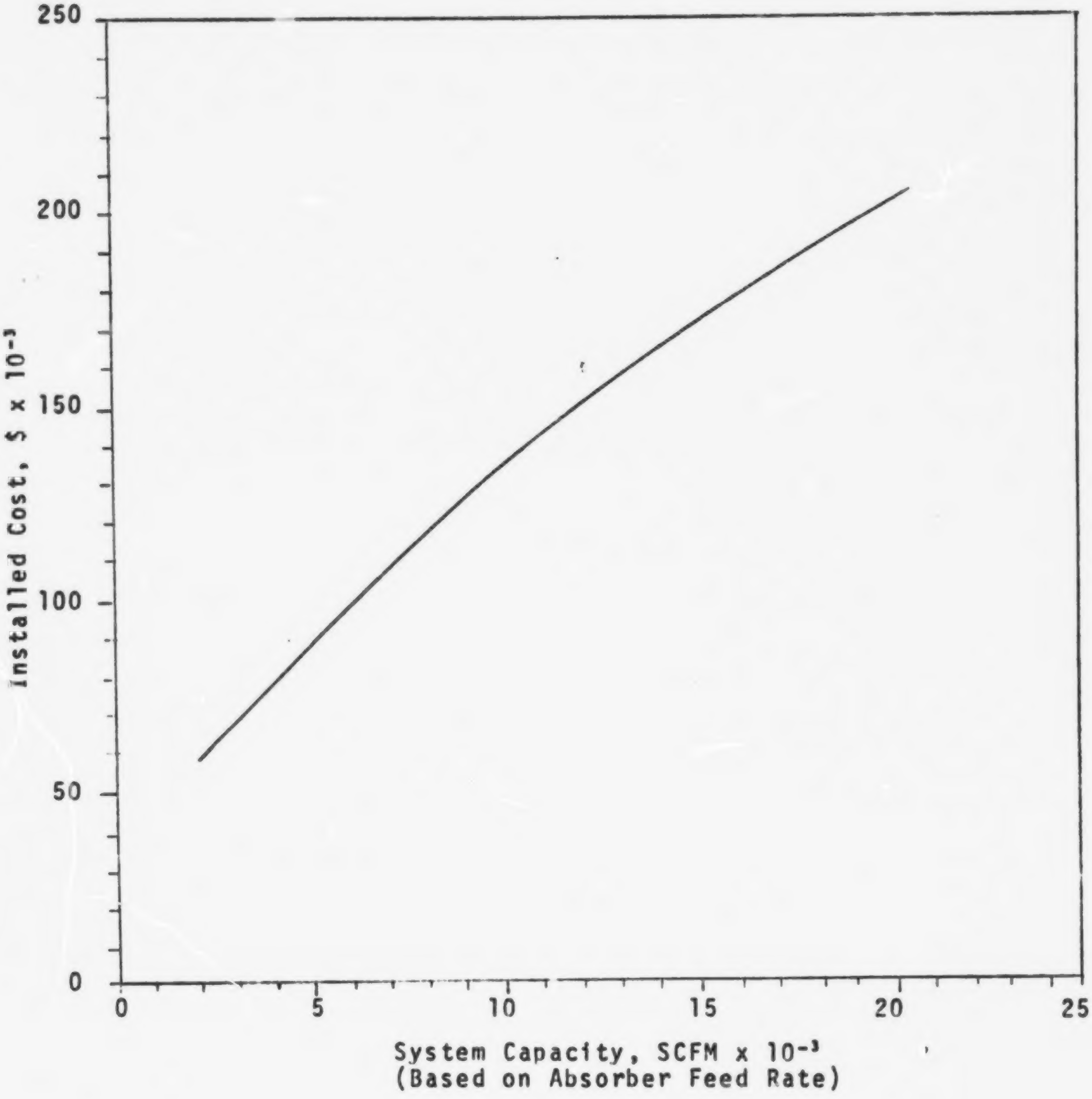

Figure VI-23 - Estimated Installed Cost of Incinerator and Absorber (Disposal of DDT/Kerosene Waste)

Payroll Overhead @ 30% Direct Labor

Plant Overhead @ 50% Direct Labor

Labor @ $4.00/hr.

Process Water @ 30¢/thousand gallons

Electricity @ $.015/KWH

Estimated operating costs for absorber feed rates of 2,000 SCFM, 10,000 SCFM, and 20,000 SCFM are summarized in Table VI-17 and plotted in Figure VI-24 as annual manufacturing cost per thousand SCF processed. These gas flows are equivalent to liquid flow rates of 100 GPH, 500 GPH, and 1000 GPH. The high operating costs of this system are the result of using the absorber water on a once-through basis. Operating cost could potentially be reduced by using a closed-loop water system for the absorber. This would require installation of a chemical treatment system, a water chilling system, and supporting process equipment.

Table VI-17 - Estimated Operating Costs of Incinerator/ Absorber Systems (Kerosene and DDT Waste)

System Capacity, SCFM (Based on Absorber Feed Rate)	2,000	10,000	20,000
Annual Operating Cost, $	32,400	123,200	232,900
Operating Cost, $/1000 SCF	.051	.033	.0314

f. Installed Cost - Scrubbing/Absorption

Process equipment costs were based on the 4000 SCFM unit actually designed. Equipment costs for other system capacities were estimated using the six-tenths factor rule defined by equation (1).

Cost of installation was estimated at 100 percent of equipment cost. Total installed costs are summarized in Table VI-18 and shown graphically in Figure VI-25; they are developed on construction cost estimate sheets in Appendix D.

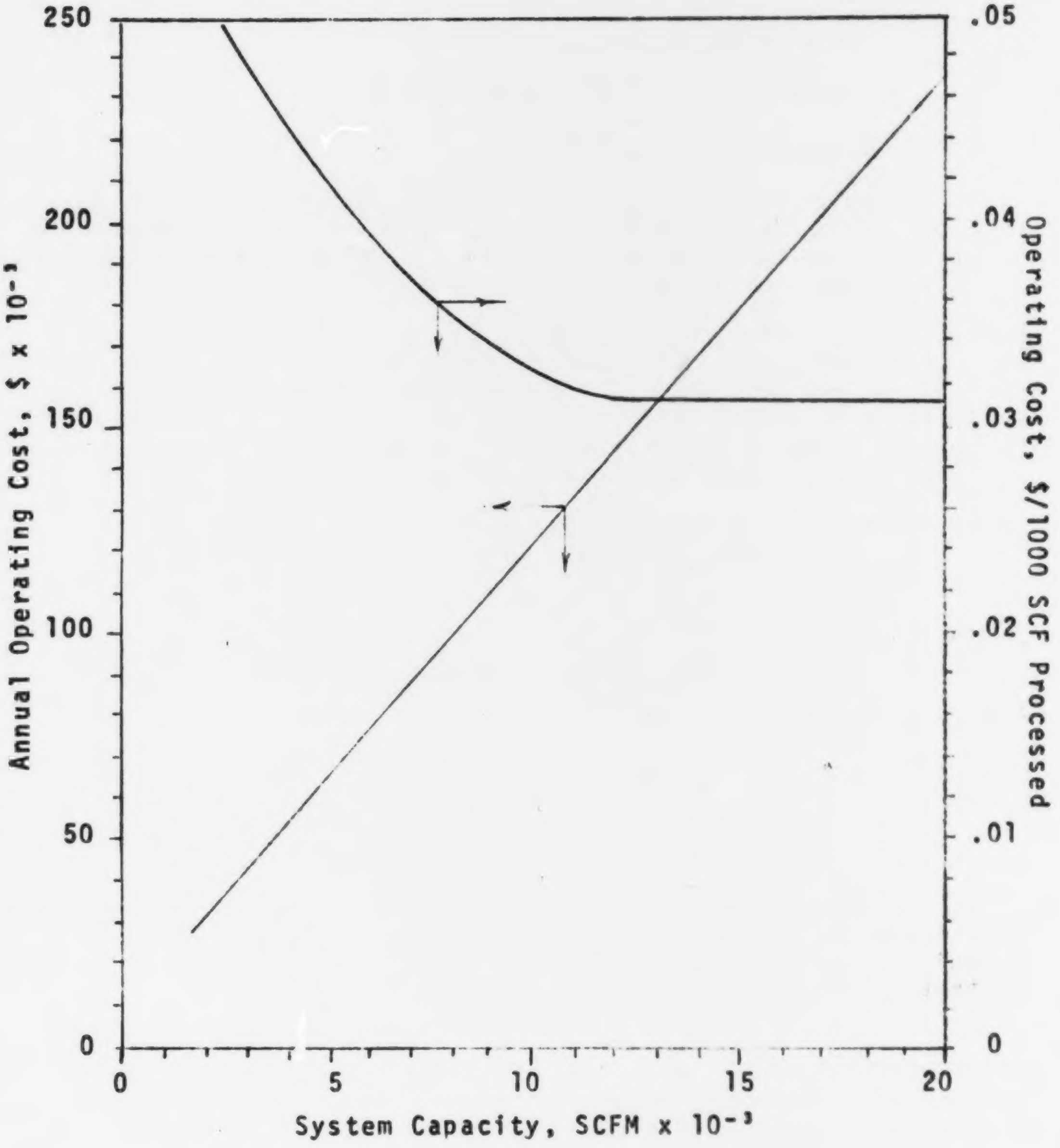

Figure IV-24 - Estimated Operating Cost of Incinerator and Absorber System (Disposal of DDT/Kerosene Waste)

Table VI-18 - Estimated Installed Costs of Scrubber/Absorber Systems (Organic Dust and Isopropanol)

System Capacity, SCFM	1,000	4,000	8,000	20,000
Installed Capital Cost, $	10,900	24,800	37,400	65,500

g. Operating Costs - Scrubbing/Absorption

Operating costs for the control system are developed on the manufacturing estimate sheets in Appendix D. Values were calculated through use of the following percentages and rates.

Operating - 2 shift/day, 330 day/year

Maintenance @ 5% capital cost

Depreciation @ 10% capital cost

Property Taxes @ 1% capital cost

Insurance @ 0.5% capital cost

Corporate Overhead @ 3% plant level cost

Supervision @ 10% direct labor

Payroll overhead @ 30% direct labor

Plant overhead @ 50% direct labor

Labor @ $4.00/hr

Process Water @ 30¢/thousand gallons

Electricity @ $.015/KWH

The operating costs are summarized in Table VI-19 and plotted on Figure VI-26.

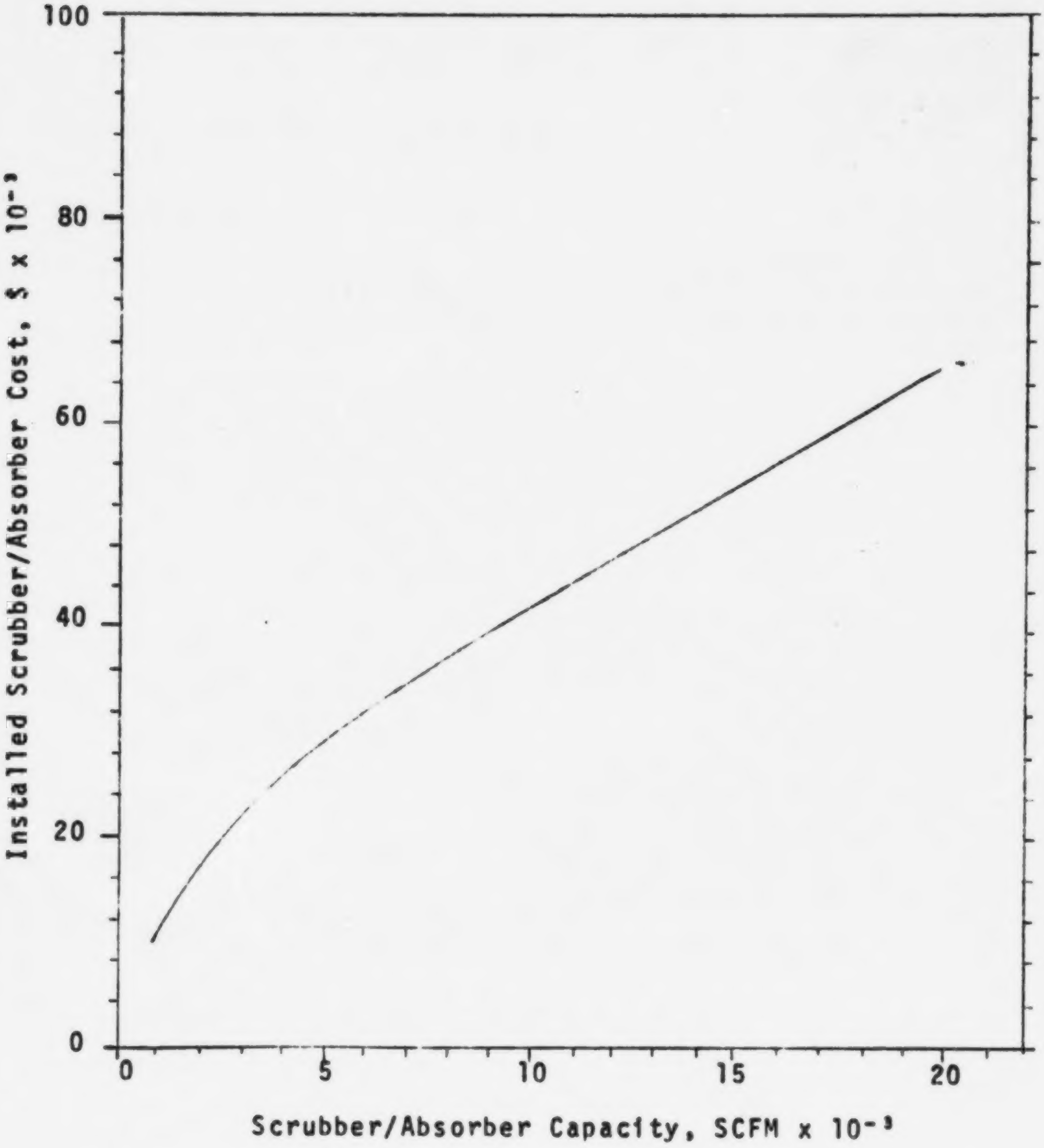

Figure IV-25 - Estimated Installed Cost of Scrubber and Absorber (Organic Dust and Isopropanol)

Table VI-19 - Estimated Operating Costs of Scrubber/Absorber Systems

System Capacity, SCFM	1,000	4,000	8,000	20,000
Annual Operating Cost, $	5,900	12,100	19,500	40,200
Operating Cost, $/1000 SCF	.019	.0095	.0077	.0063

D. GROWTH PROJECTIONS

1. General

Any consideration of the regulation and control of air pollution must take into account the projected growth (or diminution) of the various segments of the national economy that contribute to or are affected by the pollution problem. Such projections or forecasts are necessitated by several factors: (1) The sources, quantities, and types of pollutant emissions are a function of the patterns of social, economic, and technological change, and are thus time-dependent parameters; (2) the often undesirable, but nevertheless real, time lag between recognition of a problem and application of a solution requires that some estimate of the future be made; (3) The economic and technological implications of the application of controls often require incremental reduction of emissions over a period of years, in order to achieve a satisfactory level of air quality. Additionally, population and industrial growth may require increasing levels of control to maintain air quality.

The hazards of forecasting technological and economic changes are well documented. The acceleration of such changes, as seen in recent years will undoubtedly continue; thus even short-range forecasts are highly uncertain. If we are to attain future air quality standards, however, general growth trends must be recognized and allowed for in planning recommendations. The growth aspects and short-range projections of several areas of the U.S. economy are presented briefly in this section.

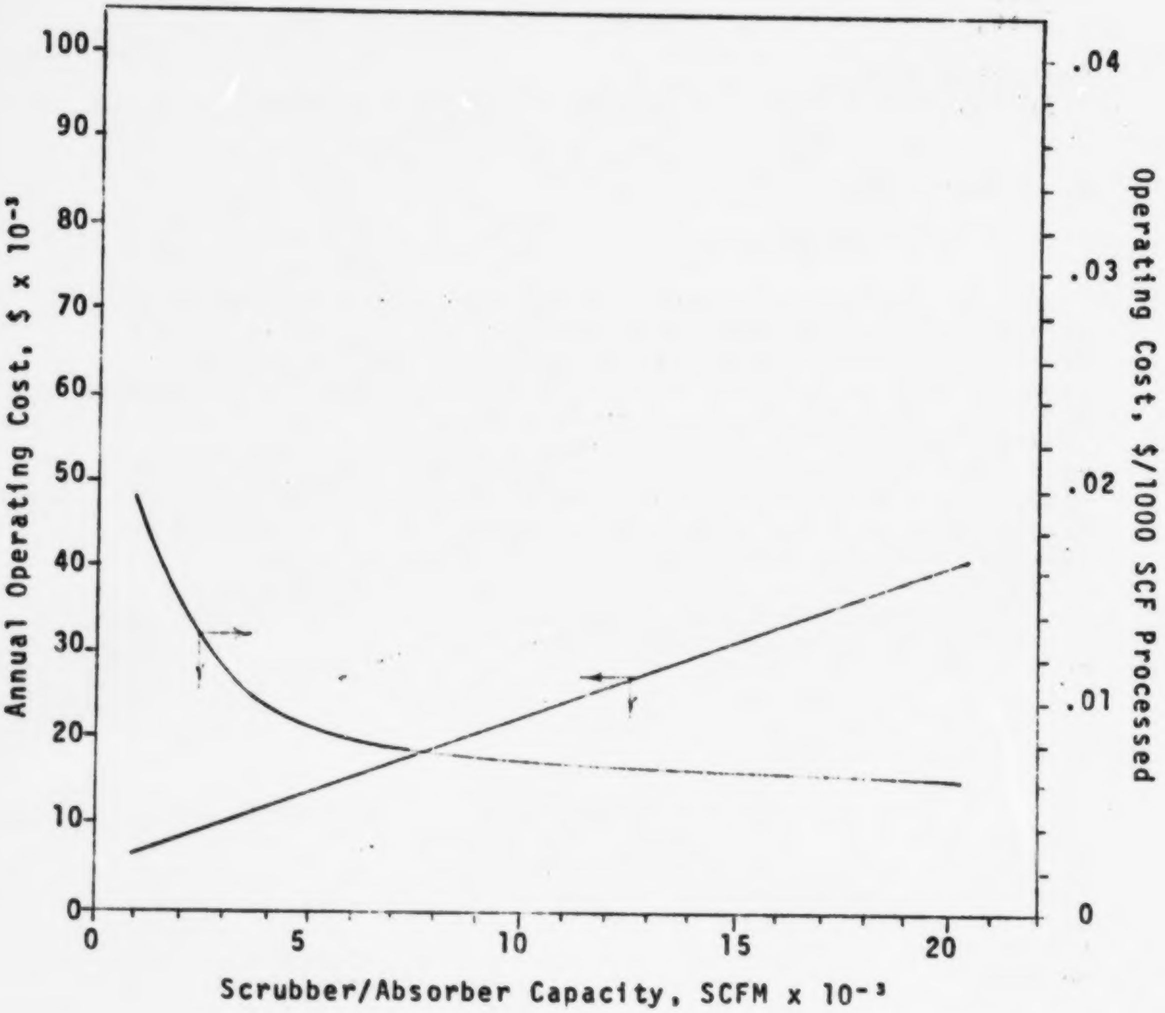

Figure VI-26 - Estimated Operating Cost of Scrubber and Absorber (Organic Dust and Isopropanol)

2. Energy Resources

A review of energy resources with projections for the future was made by Morrison (1968). This review presents a simplified energy model for the United States and, for various assumptions relating to technological changes and innovations, projects energy consumption to the years 1980 and 2000. The medium-term forecasts, along with historical data, are shown in Table VI-20 for the major sources of energy.

In spite of significant changes in nuclear energy sources, the increase in total use of fossil fuels from 1970 to 1980 is projected to be nearly 30 percent. Assuming a proportionate increase in organic emissions from fossil fuel use, if uncontrolled, the emissions from combustion of coal, oil, and gas by 1980 would reach about 0.3 x 10^6 tons/year.

In addition to the effect of increased nuclear energy sources, such factors as the increased efforts in coal gasification and oil shale usage could significantly affect these projections. A recent article (Washington Energy Memo, March 29, 1971) cited a Department of Interior projection of a possible 36 plants producing fuel gas from coal, producing 3 trillion cubic feet of gas a year. This is estimated at 10 percent of the predicted gas consumption.

3. Petroleum Industry

Martin (1970) reviewed the near future of the refining industry and presented some medium-range growth projections. Petroleum industry experts predict a total U.S. crude petroleum throughput of about double the present capacity by the mid 1980's. Construction engineering firms specializing in refinery processes project somewhat lower estimates of 14 to 17 x 10^6 bbl/day refinery throughput by 1985, from the current level of about 11 x 10^6 bbl/day.

Martin predicts that the increased throughput will be handled with no net increase, or perhaps even a decrease, in the total number of plants. Thus, new plants will be of much higher capacity and many present small units will be phased out. Although some coastal plants might attain as much as 500,000 bbl/day capacity (currently only five refineries yield more than 300,000 bbl/day), most of the industry believes that capacity of new plants will be in the range of 200,000 to 300,000 bbl/day .

Table VI-20 - United States Total Gross Consumption of Energy Resources by Major Sources*
1947-65 and Projections to 1970, 1975, and 1980[1]

(Trillion Btu)

Year	Anthracite	Bituminous and Lignite	Natural Gas Dry[2]	Petroleum[3]	Total Fossil Fuels	Hydropower[4]	Nuclear Power	Total gross Energy Inputs
Historical year:								
1947	1,224.2	14,599.7	4,518.4	11,367.0	31,709.3	1,459.0	-	33,168.3
1948	1,275.1	13,621.6	5,032.6	12,558.0	32,487.3	1,507.0	-	33,994.3
1949	957.6	11,673.1	5,288.5	12,120.0	30,039.2	1,565.0	-	31,604.2
1950	1,013.5	11,900.1	6,150.0	13,489.0	32,552.6	1,601.0	-	34,153.6
1951	939.8	12,285.3	7,247.6	14,848.0	35,320.7	1,592.0	-	36,912.7
1952	896.6	10,971.4	7,760.4	15,334.0	34,962.4	1,614.0	-	36,576.4
1953	711.2	11,182.1	8,156.0	16,098.0	36,147.3	1,550.0	-	37,697.3
1954	683.2	9,512.2	8,547.6	16,138.0	34,881.0	1,479.0	-	36,360.0
1955	599.4	11,104.0	9,232.0	17,524.0	38,459.4	1,497.0	-	39,956.4
1956	609.6	11,340.8	9,834.4	18,624.0	40,408.8	1,598.0	-	42,006.8
1957	528.3	10,838.1	10,416.2	18,570.0	40,352.6	1,568.0	1.2	41,921.8
1958	482.6	9,607.6	10,995.2	19,214.0	40,299.4	1,740.0	1.5	42,040.9
1959	477.5	9,595.9	11,990.3	19,747.0	41,810.7	1,695.0	2.2	43,507.9
1960	447.0	9,967.2	12,698.7	20,067.0	43,179.9	1,775.0	5.5	44,960.4
1961	403.8	9,809.4	13,228.0	20,487.0	43,928.2	1,628.0	17.0	45,573.2
1962	381.0	10,159.7	14,120.8	21,267.0	45,928.5	1,780.0	23.0	47,731.5
1963	361.0	10,722.0	14,843.0	21,950.0	47,876.0	1,740.0	33.0	49,640.0
1964	365.8	11,295.0	15,647.5	22,385.8	49,694.1	1,873.0	34.0	51,601.0
1965 preliminary	327.7	12,030.0	16,136.1	23,209.3	51,703.1	2,050.0	38.0	53,791.1
Projected years:								
1970	309.0	14,251.0	19,374.0	27,275.0	61,209.0	2,193.0	874.0	64,276.0
1975	280.0	16,865.0	22,360.0	31,875.0	71,380.0	2,422.0	1,803.0	75,605.0
1980	250.0	19,290.0	25,455.0	35,978.0	80,973.0	3,026.0	4,076.0	88,075.0

[1] Gross energy is that contained in all types of commercial energy at the time it is incorporated in the economy, whether the energy is produced domestically or imported. Gross energy comprises inputs of primary fuels (or their derivatives), and outputs of hydropower and nuclear power converted to theoretical energy inputs. Gross energy includes the energy used for the production, processing, and transportation of energy proper.

[2] Excludes natural gas liquids.

[3] Petroleum products including still gas, liquefied refinery gas, and natural gas liquids.

[4] Represents projections of outputs of hydropower and nuclear power converted to theoretical energy inputs at projected rates of pounds of coal per kilowatt hour at central electric stations. Excludes inputs for power generated by nonutility plants, which are included within the other consuming sectors.

Sources: Compiled by Division of Mineral Economics, Bureau of Mines, U.S. Department of the Interior, supplemented by estimates for conventional power plants and for nuclear power from the Federal Power Commission and the Atomic Energy Commission.

*From Morrison and Readling (1968)

A recent news article (Washington Energy Memo, April 5, 1971) reports an API estimate that proved recoverable crude reserves in North America totaled 39 billion barrels as of December 31, 1970. This represents an increase over the previous year of 9.4 billion. This increase, however, is due entirely to Alaskan drilling activity; the lower 48 states show a net decrease.

4. Solvents

Growth trends in solvent production and usage are upward but erratic. The impact of pollution control by such legislation as Rule 66 in Los Angeles, Regulation 3 in San Francisco, and other similar restrictions has already been noticeable in certain segments of the solvent industry. Reformulation of mixed solvents for specific applications has been one of the approaches favored by the industry for compliance with control legislation. Reformulation has not significantly changed the total solvent consumption, the net result being a decrease in the non-exempt or reactive solvents and a concomitant increase in other non-reactive components.

The use of water-base or completely solventless coatings and inks has been accelerated by pollution control regulations. For those applications, such as architectural coatings, which are not amenable to recovery or control, reformulation and increased usage of water-base paints has been the only recourse.

Recent news releases by the printing industry indicate significant progress in development of completely solventless inks for some applications.

Production of paint, varnish, and lacquer has increased from 398 million gallons in 1966 to about 445 million gallons in 1970, or about 12 percent. Similar, or even slightly increased growth may be projected for the near future. However, pressure for reduction of emissions may be expected to generally reduce the total usage of organic solvents in coatings.

The net result of industrial and population growth coupled with increased emission control efforts will be a continued overall growth rate of perhaps 4 or 5 percent per year; considerable rearrangement of the consumption of individual solvents will take place, however, reflecting the trend toward the usage of less photochemically reactive solvent blends.

5. Solid Wastes

As discussed in Chapter III, Section C, the current status of the generation and disposal modes of solid wastes is only partially defined. Thus, general forecasts, even over short time spans, are highly speculative and subjective. For municipal and domestic wastes, where there is some general agreement as to current status, the growth is expected to follow patterns of population change and demographic distribution. Added to this population-dependent growth is a variable factor reflecting an apparently accelerating rate of per capita waste generation.

Fogel et al (1970), in projections of pollution control costs, assumed this latter portion of the waste generation growth to be represented by a 3 percent per year increase. Black et al (1968), in summarizing the results of the National Solid Wastes Survey, extrapolated the per capita increase in waste production according to recent increases in consumption of durable and non-durable goods, or about 4 to 6 percent per year.

A.D. Little (1969) reported projections of solid waste generation through the year 2000. By combination of their population growth rate and refuse quantity growth rate, the total generated refuse for 1980 is projected as about 1.2 times the 1970 level.

The shifting patterns of land usage and the pressures of all types of pollution control programs will greatly affect the growth or diminution of the various disposal modes. Open burning of domestic and municipal wastes is now banned in many areas, and the number of communities applying such bans is expected to increase rapidly during the next 2 to 5 years. Open burning of industrial, commercial, and agricultural wastes is being increasingly controlled by local variance rulings. Meteorologically scheduled open burning of bulk wastes not suitably handled by other disposal methods is increasing, with a concomitant reduction of the local adverse effects, if not of the total pollution load.

6. Total Hydrocarbon Emission

Estimates of the growth rates of the total organic emissions may be obtained from comparison of emission inventories and estimates made by pollution control agencies. As an example, data are presented for the San Francisco Bay Area (BAAPCD, 1969) in which potential or uncontrolled emissions are compared with actual or partly controlled emissions. These data show an estimated reduction of potential or uncontrolled stationary source organic emissions of 1041 tons/day; a reduction of nearly 53 percent.

The Bay Area estimates also show that potential organic emissions from stationary sources would have grown from 1922 tons/day in 1955 to 1982 tons/day in 1969, for an average uncontrolled compounded growth rate of about 3 percent per year. This would forecast a doubling of organic emissions from stationary sources in about 25 years, if uncontrolled. These data show a net reduction from 1955 to 1969 of ~1500 ton/day of organic emissions from all sources, both mobile and stationary. Allowing for estimated growth of uncontrolled emissions, this shows the achievement of a reduction of potential 1969 emissions of ~5300 ton/day, or a 67 percent reduction.

The impact of such an uncontrolled growth rate may be visualized by the application of a rollback analysis to ambient air quality standards for hydrocarbons. The usual expression for a rollback calculation assumes a 1:1 relationship between the reduction in emissions and the improvement in ambient air quality and was expressed in mathematical form by Jensen (1971) as

$$A = \frac{(Q-B)}{G(U-B)}, \text{ where}$$

A = allowable emission fraction
Q = ambient air quality standard
U = present air quality
B = background
G = growth factor

For the purposes of this calculation, a current air quality level (U) may be obtained from recent CAMP data (Larsen, 1970) for total hydrocarbon concentration and the assumption that the non-methane fraction is about 40 percent of the total concentration. Thus, a typical urban non-methane hydrocarbon concentration (3 hr average) would be about 2 ppm (as C). The recommended national standard for ambient non-methane hydrocarbon (Federal Register, 1971) is 0.24 ppm (as C).

The background level (B) for non-methane hydrocarbon is difficult to define readily, but the value of 0.5 ppm (USDHEW, 1970) is not unreasonable.

Substituting these values into the above rollback expression, and applying a growth factor of 2, for the expected doubling of emissions in about 25 years, the estimated allowable emission fraction is

$$A = \frac{0.24 - 0.05}{2(2 - 0.05)} = 0.049$$

This is equivalent to a reduction in all emissions over the 25 year time span of 95.1 percent.

Even if a zero growth rate (G = 1) in emissions is projected, the necessary reduction of emissions over the time span of interest would be about 90 percent. Thus, the achievement of current air quality standards for hydrocarbons over any reasonable time span is seen to be a formidable task.

Lacking any basis for estimation of the amount and effectiveness of applied control that will be put into practice over the next few years, the only forecast that can be made is one based on uncontrolled emission growth rates. From the estimates made by San Francisco Bay Areas, APCD, the overall uncontrolled growth rate for stationary source organic emissions may be assumed to be about 3 percent per year. At this rate, the currently estimated total hydrocarbon emissions from stationary sources of 25 to 26 million tons per year would reach nearly 35 million tons per year by 1980.

In view of the assumptions, and resultant uncertainty, involved in making this overall extrapolation, more detailed estimates of future hydrocarbon emissions is unwarranted.

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VII. RESEARCH AND DEVELOPMENT RECOMMENDATIONS

A. INTRODUCTION

Current awareness of the problems associated with pollution of our environment has resulted in the development of federal, state, and local programs to identify, assess, and control emissions that have adverse effects on our society and economy. This present study was one of many such programs sponsored by the Environmental Protection Agency having the ultimate goal of providing problem-solving research and development programs to aid in future planning for governmental action.

The R&D program developed from this study was based on results of the review of the sources, emissions, adverse effects, and control of hydrocarbon pollutants. Evaluation of these results in terms of priorities, economic impact, and data needs resulted in the formulation of detailed R&D recommendations.

These recommendations include objectives, priorities, technical effort, and estimated cost for needed studies in the following areas:

1) Definition and quantification of the adverse effects of hydrocarbon pollutants, particularly those related to human health.

2) Characterization of hydrocarbon emission streams, relative to chemical composition and engineering control design parameters.

3) Development of cost/benefit data for total systems analysis.

4) Correction of deficiencies in control technology, emission characterization and monitoring, and feasible alternatives for reduction of total environmental pollution.

B. R&D PRIORITIES AND NEEDS

1. Application of Existing Technology

Significant reduction in the emissions of atmospherically reactive hydrocarbons and, concomitantly, diminution of the impact of the most widely recognized adverse effect, photochemical smog, can be achieved by application of existing control techniques and alternatives. This fact has been amply proven by the experience of local pollution control agencies in the major smog areas of California.

For the most immediate short-range benefit, implementation of available technology must be given high priority. Control or restriction of the use of photochemically reactive solvents, limitations or bans on open burning of wastes, and control of evaporative losses during gasoline storage and marketing, when coupled with the current implementation of mobile emission source controls, would result in significant benefits to that majority of the populace now centered in major metropolitan areas.

The impact of existing controls on the industrial sector of the economy has not proved to be the severe hardship expected by many. Experiences with such controls on the West Coast have not significantly affected overall economic growth, although in certain instances adjustments and modifications did pose some difficulty. Our limited investigation of general-case control systems showed that economic payouts or benefits can result,in some cases, from the application of controls. These findings are supported by numerous industrial case histories reported in the literature.

Thus, although it does not directly relate to our R&D planning objectives, the highest priority in terms of direct benefit to society must be the rapid implementation of existing control technology.

2. Updating Existing Literature on Control Technology

Relevant to the short-range benefits achievable by application of existing technology is the need for updating much of the published information on design and application of control systems. Although much helpful information can be obtained through data and services provided by individual experts, and from engineering and equipment firms specializing in pollution control, the published literature is woefully inadequate for the engineer faced with a specific problem.

High priority thus should be placed on updating and revising the existing texts and manuals to provide meaningful basic design and engineering data for practicing industrial pollution control engineers and for control agency personnel responsible for the specification and approval of control installations. The Air Pollution Engineering Manual (Danielson, 1967) made an excellent approach toward providing such information and, thus, could serve as a model for revision and updating. The revised manual should be in a format suitable for periodic addenda provided by a continuing program of data compilation and evaluation.

3. Pollutants and Effects

Although evidence relating hydrocarbons to photochemical smog is sufficient to require corrective action, studies of the health effects of chronic exposure to specific organic compounds and mixtures thereof should be conducted. The results of such studies, combined with the fragmented data available in the literature, would provide the information necessary to adequately protect society from unknown or suspected but unproven hazards arising from long-term exposure to organic species not eliminated by smog control action.

To support such health studies, more detailed characterization of specific source emissions of organic compounds is required. For even the most thoroughly studied emission sources, published data are barely adequate to allow estimates of total organic emissions; detailed characterization of organic emissions as to chemical composition and concentration ranges is almost entirely lacking. To accomplish these studies, improvements in analytical techniques and equipment would be highly desirable. Particular emphasis should be placed on the development of discriminatory continuous monitoring techniques, since grab sample and spot check tests of emission sources can yield highly erroneous and conflicting results.

Recent investigations of the photochemical reactivity of hydrocarbons that were previously considered unreactive have shown that smog manifestations can be produced in laboratory experiment with even completely saturated paraffinic hydrocarbons. Investigations of this type, over wide ranges of experimental conditions, should be continued. These studies, as well as investigations of synergistic interactions, would further our knowledge of the critical control steps required for elimination of photochemical smog.

4. Control Technology Improvements

Recognizable deficiencies in current control technologies must be corrected if long-range plants to eliminate hydrocarbon pollution are to be realized. Significant areas for study are:

1) Afterburners - studies of both direct-fired and catalytic systems to better define control effectiveness and to improve combustion efficiencies.

2) Wet Scrubbers - data correlation and appropriate experimental studies to correlate performance data and improve design bases.

3) Adsorption - selected experimental studies to better system design bases and to widen the range of applicability.

4) Storage Tank Controls - studies to update data base for estimation of losses and to investigate usage of novel materials as sealants.

5) Dry Particulate Collectors - collection and analyses of performance data on the removal of polycyclic aromatic hydrocarbons.

5. Water and Solid Waste Pollution

Existing technology for the control of hydrocarbon air pollutant emissions often simply transfers pollutants from one facet of the environment to another; thus control of air pollution can create problems of water pollution or of solid waste disposal. Programs directed toward control of hydrocarbon air pollutants should be integrated with the overall environmental pollution control objectives. Studies of air pollutant control devices that create potential water or solid waste problems should be implemented. Particular areas for study are the clarification, neutralization, and recycle or disposal of wet scrubber liquors and the disposal of organic particulates which may result in potential carcinogenic hazard.

The need for interdisciplinary correlation of control programs is pointed up by the significant amounts of hydrocarbon air pollutants emitted by the indiscriminate disposal of solid or liquid wastes. Control planning for such waste disposal must consider the potential side effects of even trace concentrations of organic emissions to the atmosphere.

C. ECONOMIC IMPACT OF CONTROL PLANNING

To achieve a realistic balance between our presently undesirable lack of emission control and the extreme of complete prohibition at any cost, the economic impact of control planning on the various sectors of society must be considered. Certain aspects of the socio-economic relationships were presented in the discussion of applications of existing controls (VII. B.1) and in Chapter V on systems modelling.

Determination of the cost of control for specific cases presents only a portion of the total picture. To complete the picture, the benefits to society resulting from control application should be assessed. Unfortunately, the lack of data quantifying the costs of adverse effects (or, conversely, the benefits of control) effectively prevents this assessment.

Attempts to estimate total costs of control for all emissions or even for any significant segment or source category are felt to be fruitless. The wide range of sizes and types of individual sources and control devices within any broad category, coupled with the lack of data on extant controls, prohibits meaningful estimates.

To even qualitatively assess, in the light of present knowledge, the impact of controls on the economy, recourse must be made to the experiences of those few regional areas having a history of applied controls. The best indication of economic cost and benefit related to control of hydrocarbon emission may be derived from studies of the Los Angeles and Bay Area control districts. Significant reductions in potential or uncontrolled emissions of hydrocarbons from stationary sources have been achieved with little or no effect on economic growth of the areas.

For example, data from the Bay Area APCD indicate that potential organic emissions from stationary sources in 1969 were reduced by about 53 percent by the application of controls. The estimated dollar cost of applied control of stationary source organic emissions in the Bay Area was about $200 million, equivalent to nearly $50 per person living in the area. The cost per annual ton of organic emission prevented by control was estimated from these data to be about $525. The cost of complete reduction of emissions was estimated by BAAPCD to be double the current total cost, or about $400 million.

Economic indicators and projections for the San Francisco AQCR (Office of Business Economics, 1970) show that total personal income and earnings from industrial employment for the region both increased about 16 percent during the period 1967 to 1970. Similar figures for the total U.S. are 15 and 14 percent, respectively.

For the Los Angeles AQCR, which is under similarly stringent control, increases in personal income and industrial earnings for the 1967-1970 period were both nearly 17 percent.

D. R&D PROGRAMS

Specific recommended programs of research and development are based on the needs and priorities identified in this study.

1. Emissions and Sources

A series of programs is needed to further define and characterize selected emissions in terms of their chemical composition, source-dependent engineering control parameters, and atmospheric distribution.

a. Program D-1a - Characterization of Selected Emissions and Sources

Objective - To provide detailed chemical and engineering data characterizing emissions from selected sources.

Discussion - Emissions and sources requiring more detailed study include all types of waste combustion, fuel combustion, and industrial processes such as coke manufacture, rubber and plastics processing, synthetic organic chemical processing, and surface coatings application and processing. Results of these studies would provide input for adverse effects studies and control systems design.

Priority - High

Duration - 3 years

Effort - 12 man-years, $600,000.

b. Program D-1b - Atmospheric Modeling

Objective - To improve procedures for relating emissions to ambient air quality.

Discussion - Existing models and mathematical techniques for estimation of ambient air distribution of emissions are limited in their ability to treat real atmospheric conditions and interactions. Because of the apparent key role of hydrocarbons in smog formation, realistic modeling to account for atmospheric reactions must be developed. Theoretical studies should be implemented by additional atmospheric monitoring studies to better define the relationships of hydrocarbons and photochemical oxidants.

Priority - Medium to high

Duration - 5 years

Effort - 10 man-years, $500,000.

c. Program D-1c - Analytical Development

Objective - To develop improved instruments and techniques for continuous monitoring of both emission sources and ambient air.

Discussion - Current monitoring techniques are limited in their ability to provide continuous, realtime determination of specific organic species or chemical groups. Laboratory development and field testing studies are needed to provide improved methods of monitoring.

Priority - High to medium

Duration - 3 years

Effort - 6 man-years; $300,000.

2. Adverse Effects

A series of programs is needed to supplement existing limited data on the adverse effects of hydrocarbon pollutants. Particular emphasis should be placed on human health effects and on assessment of economic costs to all sectors of society.

a. Program D-2a - Animal Toxicity Studies

Objective - To provide data on both short-term and chronic exposures for assessment of health effects of hydrocarbon pollutants.

Discussion - Limited data on health effects of low concentrations of hydrocarbons should be supplemented by laboratory toxicity studies of animals. Of particular importance are investigation of the effects of exposures to polycyclic aromatic hydrocarbons, oxygenated hydrocarbons, and photochemical smog products.

Priority - High

Duration - 3 years

Effort - 6 man-years; $350,000.

b. Program D-2b - Epidemiological Studies

Objective - To provide statistically validated correlations of hydrocarbon pollutants and human health.

Discussion - Field data on urban and non-urban population samples should be compiled and analyzed. Areas and population samples selected should provide ranges and extremes of exposure. Particular emphasis should be placed on the inter-relationships of exposures with predisposing health conditions and synergistic factors.

Priority - Medium to low

Duration - 5 years

Effort - 3 man-years; $175,000.

c. Program D-2c - Smog Studies

Objective - To compile and analyze data on human response to both actual and synthetic smog atmospheres.

Discussion - Smog chamber studies, coupled with field data compilation, are needed to establish human responses to exposures over wider ranges of time and concentration. Synthetic atmospheres should be developed to correspond with the range of actual exposures in polluted atmospheres.

Priority - Medium

Duration - 3 years

Effort - 6 man-years; $300,000.

d. Program D-2d - Economic Costs

Objective - To compile and analyze field data on economic costs of hydrocarbon pollutants.

Discussion - To completely analyze cause and effect relationships, better data are needed on the economic costs of the effects of hydrocarbon pollutants. Costs of health effects and of damage to vegetation and materials should be developed and analyzed. Field survey teams would compile data for input to a cost - benefit model analyses.

Priority - Medium

Duration - 3 years

Effort - 6 man-years; $300,000.

3. Control Systems

A series of programs is recommended to improve the design bases, (assessment of control effectiveness and implementation of control systems.

a. Program D-3a - Control Effectiveness of Direct Flame Afterburners

Objective - To compile and analyze data on the control effectiveness or control efficiency of currently utilized systems.

Discussion - To implement more effective use of direct flame afterburners, studies should be made, under typical field conditions, of the control effectiveness or efficiency of these systems. Studies would include analysis of influent and effluent contaminant concentrations as a function of the combustion parameters (flow rate, residence time, temperature and fuel and air rates). Detailed cost data should be compiled and analyzed.

Priority - High

Duration - 1.5 years

Effort - 4 man-years; $200,000.

b. Program D-3b - Control Effectiveness of Catalytic Afterburners

Objective - Same as D-3a, but for catalytic systems

Discussion - Same as D-3a, but for catalytic systems

Priority - High

Duration - 1.5 years

Effort - 4 man-years; $200,000.

c. Program D-3c - Improved Afterburner Designs

Objective - To improve the combustion efficiency of both flame and catalytic afterburners.

Discussion - This program would consist of several phases of study to improve current designs of afterburners systems: a theoretical and laboratory study of combustion chamber configuration, utilizing flow modeling techniques developed for combustion furnace design; laboratory and pilot scale studies of novel designs under simulated operating conditions; field testing of best design configurations.

Priority - High

Duration - 2 years

Effort - 5 man-years; $350,000.

d. Program D-3d - Adsorption Systems

Objective - To improve existing design base for carbon adsorption systems.

Discussion - Existing design bases for activated carbon adsorption system should be updated, particularly by studies of adsorption and desorption of over a wider range of operating conditions. Studies to collect and compile such operating data should also be complemented by engineering cost data.

Priority - Medium

Duration - 1.5 years

Effort - 3 man-years; $150,000.

e. Program D-3e - Wet Scrubber Systems

Objective - to develop improved design base for wet scrubbers systems.

Discussion - A three-phase program is recommended to provide, ultimately, a sound engineering design base for selection and operation of wet scrubbers for particulate removal. The study phases are 1) further compilation and correlation of existing test data in context of correlation with agglomeration index; 2) theoretical model development; 3) experimental performance studies to confirm correlation and theory. Results should be complemented by detailed cost studies of selected devices.

Priority - High

Duration -	Phase 1)	0.75 year
	Phase 2)	1 year
	Phase 3)	2 years
	Total	3.75 years

Effort -	Phase 1)	1 man-year;	50,000
	Phase 2)	0.5 man-year;	$25,000
	Phase 3)	6 man-years;	$400,000
	Total		$475,000

f. Program D-3f - Dry Collectors

Objective - To analyze performance of dry particulate collectors with respect to removal of condensed-phase polycyclic aromatic hydrocarbons (PAH).

Discussion - PAH and other condensible hydrocarbons are known to be associated with particulate emissions. The performance of dry particulate collectors should be analyzed for effectiveness in PAH removal, particularly from combustion sources.

Priority - Medium

Duration - 1.5 years

Effort - 3 man-years; $150,000.

g. Program D-3g - Storage Tank Controls

Objective - To update data base on control effectiveness and to investigate new or novel materials for roof seals.

Discussion - The existing data base for control effectiveness of floating roof controls on storage tanks is considerably outdated. A cooperative industry-government program would provide input to update loss calculations. A second phase of the study would experimentally investigate the potential of novel materials as improved roof seals.

Priority - Medium to low

Duration - Phase 1) 3 years
Phase 2) 1 year

Effort - Phase 1) 1.5 man-years; $75,000
Phase 2) 1 man-year; $75,000

h. Program D-3h - Vapor Recovery Systems

Objective - to provide engineering and cost data on vapor recovery systems

Discussion - Existing data on vapor recovery systems are quite limited. Compilation and analysis of engineering performance and cost data are required.

Priority - Medium to low

Duration - 0.75 year

Effort - 1 man-year; $50,000.

i. Program D-3i - Engineering Manual

Objective - To revise and update control engineering manual

Discussion - A program is recommended to revise and update the Air Pollution Engineering Manual, with provision for a continuing program of revision to maintain currency of data.

Priority - High

Duration - 5 years

Effort - 2.5 man-years; $250,000

4. Water and Solid Waste Studies

The inter-relationship of air pollution with water and solid waste pollution requires careful analysis of air pollution control devices to avoid creating other pollution problems.

a. Program D-4a - Wet Scrubber Waste Disposal

Objective - To prevent problems of water pollution or solid waste disposal from operation of wet scrubber devices for air pollution control.

Discussion - The suggested program should review current problems of waste disposal from wet scrubbing operations and investigate new or improved techniques for neutralization, recycling or disposal of scrubber liquors. Cost analyses of disposal or treatment should be applied to control system cost evaluation.

Priority - Medium

Duration - 2 years

Effort - 5 man-years; $250,000.

b. Program D-4b - Dry Collection Waste Disposal

Objective - Similar to D-4a

Discussion - Specific emphasis should be placed on determination of potential hazards from disposal of wastes having high PAH content.

Priority - Medium

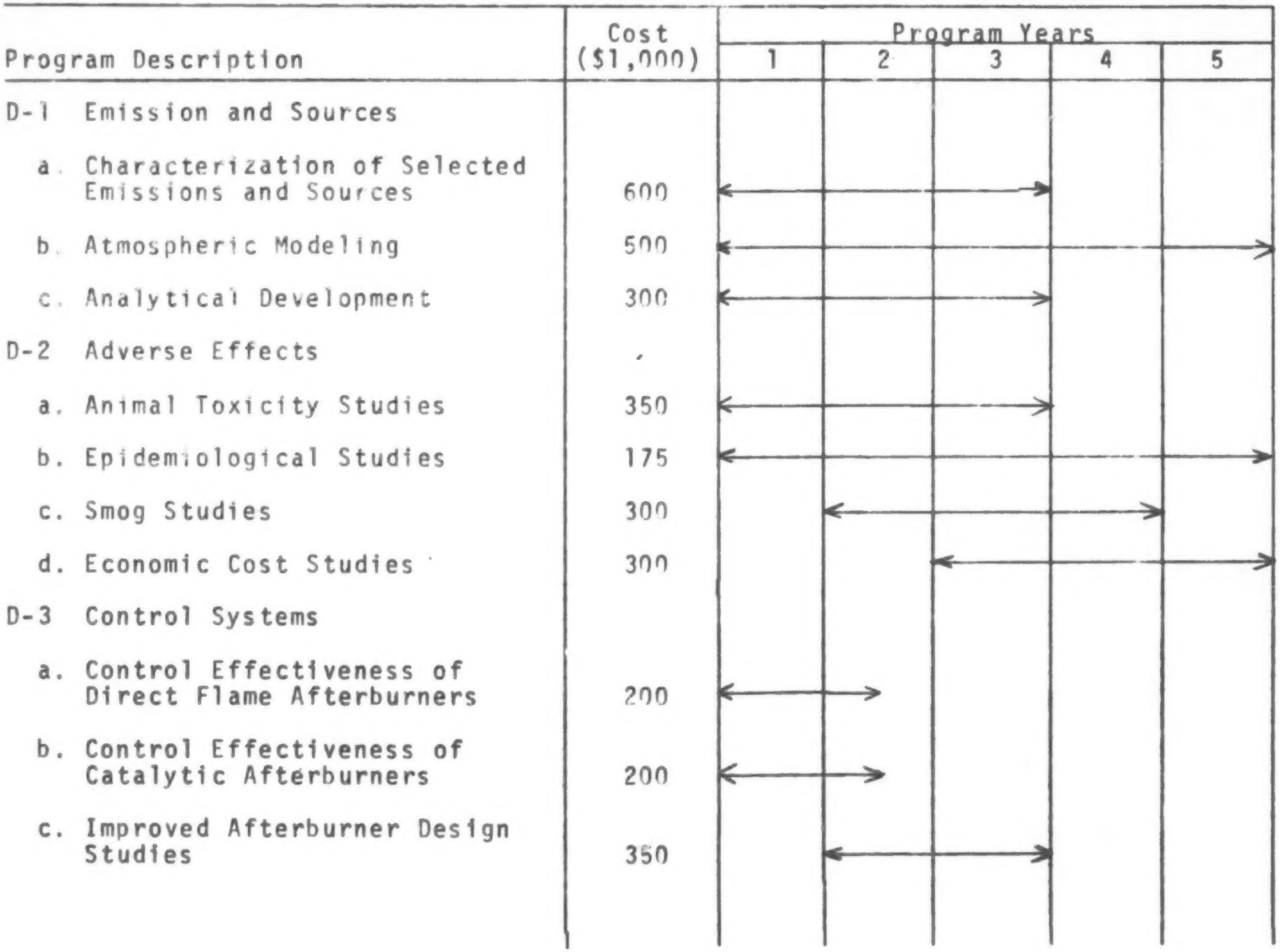
Duration - 2 years

Effort - 5 man-years; $250,000.

e. Milestone Schedule

Figure VII-1 provides a suggested milestone schedule for the 5-year, $5 million R&D program described in the previous section (VII-D).

Figure VII-1 - Milestone Schedule for 5 Year, $5 Million R&D Program



Program Description	Cost ($1,000)	Program Years 1	2	3	4	5
D-1 Emission and Sources						
a. Characterization of Selected Emissions and Sources	600	←	—	→		
b. Atmospheric Modeling	500	←	—	—	—	→
c. Analytical Development	300	←	—	→		
D-2 Adverse Effects						
a. Animal Toxicity Studies	350	←	—	→		
b. Epidemiological Studies	175	←	—	—	—	→
c. Smog Studies	300		←	—	→	
d. Economic Cost Studies	300			←	—	→
D-3 Control Systems						
a. Control Effectiveness of Direct Flame Afterburners	200	←	→			
b. Control Effectiveness of Catalytic Afterburners	200	←	→			
c. Improved Afterburner Design Studies	350		←	→		

Figure VII-1 (continued)

Program Description	Cost ($1,000)	Program Years 1	2	3	4	5
d. Adsorption System Design Studies	150		←	→		
e. Wet Scrubber Systems Studies						
Phase 1	50	→				
Phase 2	25	↔				
Phase 3	400		←	→		
f. Dry Collector Studies	150			←	→	
g. Storage Tank Controls						
Phase 1	75		←	—	→	
Phase 2	75					↔
h. Vapor Recovery Systems	50				↔	
i. Engineering Manual	250	←	—	—	—	→
D-4 Water & Solid Waste Studies						
a. Wet Scrubber Waste Disposal	250				←	→
b. Dry Collector Waste Disposal	250				←	→
TOTALS	5,000	910	1,310	1,360	860	560